THE PREPARATION AND X-RAY CRYSTALLOGRAPHIC STUDY OF SEVERAL ION-EXCHANGED, COMPLEXED SYNTHETIC ZEOLITES

A SENIOR HONORS THESIS SUBMITTED TO THE FACULTY
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If he (the teacher) is indeed wise
he does not bid you enter the house
of his wisdom, but rather leads you
to the threshold of your own mind.

Kahlil Gibran

The author gratefully acknowledges his advisor, Dr. Karl Seff. His supervision has made this research a unique and rewarding experience.

I am also indebted to Allen Amaro, Dr.Roger Cramer, Cathryn Kovaciny, Paul Riley, and Russell Yanagida for their assistance, and to L.L.Y.Chun and J.Niwa for the synthesis of some of the zeolite A used in this work.

ABSTRACT

Zeolitic ion-exchange experiments were carried out using Au^{+3}, Ag^{+2}, Ca^{+2}, Cr^{+3}, Co^{+2}, Cu^{+2}, Fe^{+2}, Mn^{+2} and Zn^{+2} solutions. Five ion-exchanged samples of the synthetic zeolite A, $Na_{12}Al_{12}Si_{12}O_{48}$, were exchanged stoichiometrically. They are;

$$Cu_2Na_8Al_{12}Si_{12}O_{48} \quad (1)$$

$$Ca_2Na_8Al_{12}Si_{12}O_{48} \quad (2)$$

$$Co_4Na_4Al_{12}Si_{12}O_{48} \quad (3)$$

$$Mn_{4.5}Na_3Al_{12}Si_{12}O_{48} \quad (4)$$

and $$Zn_5Na_2Al_{12}Si_{12}O_{48} \quad (5).$$

The selenium and tellurium sorption complexes of zeolite A, zeolite (2), and zeolite (3) were also prepared.

The crystal and molecular structure of the selenium sorption complex of (2), $Se_8Ca_2Na_8Al_{12}Si_{12}O_{48}\cdot XH_2O$, and the hydrated form of (5), $Zn_5Na_2Al_{12}Si_{12}O_{48}\cdot 29H_2O$, were studied by X-ray diffraction techniques.

The selenium sorption complex was found to be crystallographically disordered.

A successful structure determination was achieved for the hydrated zinc-exchanged zeolite, and was refined to R_1 and R_2 error indices of 0.097 and 0.092, respectively.

The methods used for ion-exchange, zeolite complexation, and crystallographic investigation are discussed. The molecular geometries for the hydrated zinc-exchanged zeolite are presented.

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The eternal mystery of nature is its comprehension.

Albert Einstein

I. INTRODUCTION

A. Rationale

The rationale behind intricate and sophisticated chemical research often eludes the layman and the scientist alike. It is of value, therefore, that the relevancy of this present endeavor be offered at the onset.

All research, but particularly novel chemical, biochemical, and physiochemical research, is hampered by the inability of many methods of experimentation to confine a problem within a closed, tightly controllable system. It is unknown or spontaneous variables which often are responsible for extending or perplexing any specific inquiry. In most cases, adequate, even applicable, understandings will not be entirely satisfactory until they account for the primary operational basis of the system to which the scientist directs his investigations.

There is perhaps no better example of this than in human biology. Early medical science could identify only blood, bone, and flesh. Later the organs were recognized and identified. Eventually a cellular theory of life was conceived. All of this knowledge was magnificently insufficent, however, in explaining and in coping with disease. Nor did it offer much aid in explaining or propagating health. It was, relatively, only recently that research restricted to <u>in vitro</u>, closely controllable, biochemical systems was able to yield suitable explainations for disease or health symptoms which are, primarily, chemical in origin. The universal use of medicinal drugs bears testimony to the reality of a concept of life based on chem-

ical foundations. It is distressfully apparent, nevertheless, that the extent of this chemical knowledge is neither deep nor broad enough.

Unfortunately, there have been no witnesses to lifes chemical construction and evolution, and we have thus been denied a complete understanding of the mechanisms by which we function. Hence, present day researchers must assume the role of archaeologists in reconstructing the molecular basis of life.[1,2,3]

It is doubtful whether many scientists apply themselves, individually, to the task of comprehending life. More likely, they restrict their work to realistic, less complex, more controllable facets of nature. In such a manner the research presented here has been confined to controllable systems, so that a submicroscopic basis for the understanding of the macroscopic, physiochemical parameters, properties, and interactions within these systems may be gained.

B. The Biological Elements

It has been established that at least 24 of the 90 naturally occurring chemical elements are essential to all living organisms.[4] These elements include manganese, iron, cobalt, copper, zinc and the monoatomic cations of sodium and calcium. The former five elements are all transition metals which life requires only in trace amounts. Because of their readily variable oxidation states and their ability to form strong complexes with ligands, these elements act as catalysts in organic and inorganic reactions.

In living organisms these trace elements often occupy allosteric sites in enzymatic metalloproteins. Manganese is found in Arginase, responsible for urea formation, and Pyruvate Carboxylase, an enzyme of pryuvate metabolism. Zinc is found in Carbonic Anhydrase, Carboxypeptidase and Alcohol De-

hydrogenase, respectively responsible for regulation of body acidity, protein digestion and alcohol metabolism. Cobalt appears in enzymes involved in the biosynthesis of DNA and in amino acid metabolism. Elasticity of aortic walls and skin pigmentation are included in the range of functions of the copper containing enzymes. Lastly, iron is a required component of the well studied proteins hemoglobin, which facilitates oxygen transport, and Succinate Dehydrogenase, a key enzyme in the aerobic oxidation of carbohydrates. The existence of interactions between these trace elements and molecular entities within living systems is thus not in doubt.

In the inorganic state, these elements appear in many minerals, exist in continental deposits, and may be found in many forms in the oceans and on the ocean floors.

Industrially, man has taken advantage of their catalytic properties to commercially produce life supporting substances. The use of transition metal complexes by the petroleum industry in catalytically producing energy rich hydrocarbons,[5] attests to the significance which these elements possess in the support of our species.

The monoatomic cations Na^+ and Ca^{++}, together with K^+, Mg^{++}, and Cl^-, are also critical to a number of functions within living organisms. They help maintain electrical neutrality of cells and fluids, play a part in maintaining the proper liquid balance of the blood and other fluid systems, and are critical to the proper functioning of the cell membrane in controlling electrochemical balances, osmotic pressure differentials, and transport of molecules into, and out of, the cell.

Much attention and investigation has been focused on the aforementioned elements and processes. The ability to create authentically modeled, yet simple, systems which may elucidate characteristics and properties of any com-

ponent of these processes, has been the key to their successful research.

The present research is directed at a deeper understanding of several of these essential elements. In their ionic form these elements, exchanged into rigid crystalline, open anionic framework structures, can be expected to display unusual coordination and to exhibit unusual chemical properties. Further, in zeolitic frameworks, the ions may have coordination sites which are not occupied and not blocked, but rather entirely vacant and available for further complexation. Substrate or ligand species may then be introduced into the zeolite cavities. The subsequent cryatallographic study of the exchanged ion - sorbed species interactions may provide insight to the role of the particular ions in biological processes. Additionally, the study of these intrazeolitic complexes is relevant to petrochemical catalysis.

C. Zeolites

The use of zeolites in this work requires that they be briefly discussed.

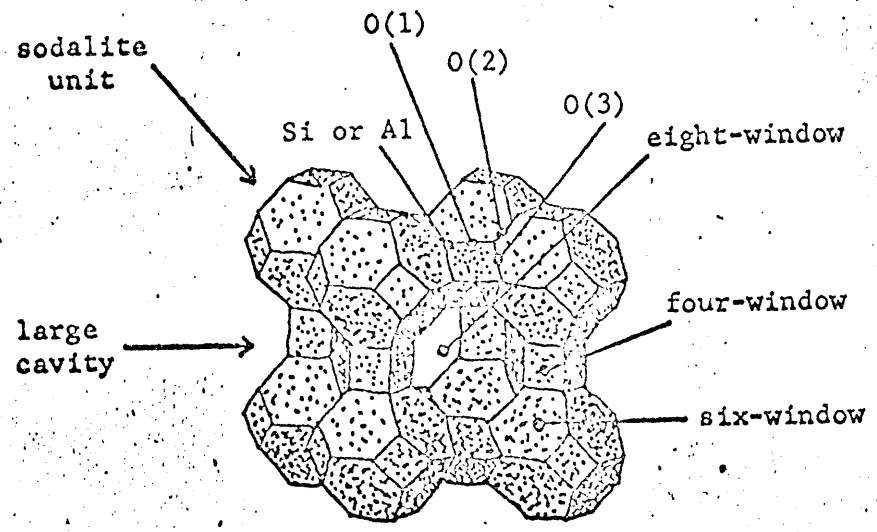
Natuarally occurring zeolites have been known since the 18th century, when the Swedish mineralogist Baron Cronstedt[6], observing that these minerals intumesce when heated, gave them their name from the Greek zeo, meaning to boil, and lithos, meaning stone. Since then mineralogists have classified over 50 types of zeolites, each with its own crystal structure. Zeolites are a class of aluminosilicates characterized by a network of SiO_4 and AlO_4 tetrahedra. The Si/Al ratio varies upward from unity depending on the zeolite type. The aluminosilicate framework is anionic and achieves neutrality through the inclusion of exchangable cations. The arrangement of the SiO_4 and AlO_4 tetrahedra gives rise to channels and cavities within the zeolite. It is into such spaces that small molecules

can be sorbed and interact with the cations. It has been hypothesized that natural zeolites could have been involved in the abiotic events leading to the origin of life.[7]

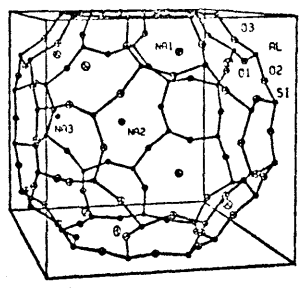
Zeolites have only in the past few decades been synthesized in the laboratory. This synthesis, initially achieved by D.W.Breck at the Linde Company,[8] has stimulated extensive research into their use as molecular sieves.[9] In this capacity their most well known use is in the softening of "hard water" by exchanging Na^+ for various divalent cations, such as Ca^{++} and Mg^{++}. Zeolites are utilized in industry to purify products by the removal of trace pollutants and to perform separations by the selective sorption of smaller or more polar molecules.[10] A significant example of their pollutant removal capacity is in their recovery and purification of radioactive cesium-137 from nuclear power sources.[11] Zeolites are also extensively used as catalysts in hydrocarbon rearrangements. When dehydrated, zeolites become the most effective desiccators known, and have been employed in high vacuum systems and in the biological dehydration and degradation of cell organelles.[12,13,14] Numerous other uses of zeolites, including those in this research, stem from their distinctive properties of high capacity ion exchange, strong and selective sorption at low sorbate concentrations, and specific catalysis.

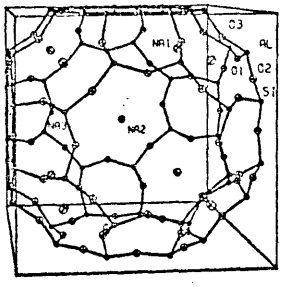
The structure of the first synthetic zeolite, type A: $Na_{12}Al_{12}Si_{12}O_{48}$, was determined by Reed and Breck[15] in 1956 and further refined by Broussard and Shoemaker[16] in 1960.

The structure of type A, a unit cell of which is shown on the next page, can be described as an assemblage of sodalite[17] cages, 6.6A in diameter, each consisting of 24 Si^+ or Al^+ ions bridged by 36 oxygen atoms. The sodalite units are, in type A, arranged in a primitive cubic array linked together by 12 additional oxygen atoms. At the center of each cube of sodalite units, a large cavity, 11.4A in diameter, is formed. In the middle of each square

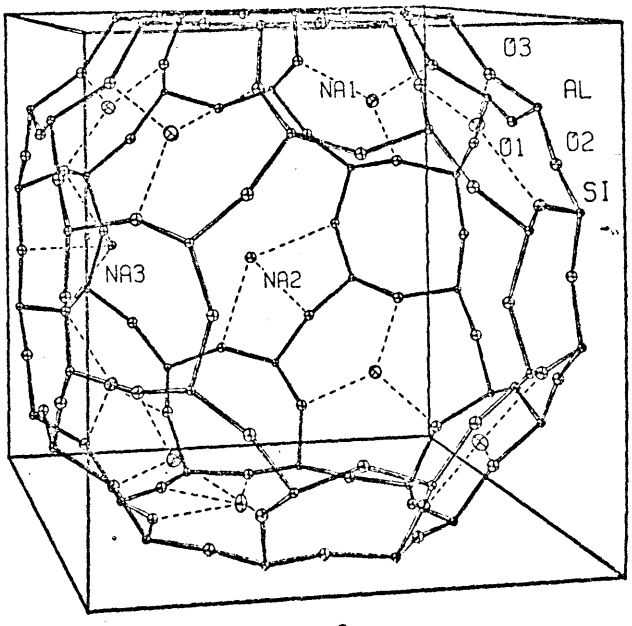


A.





B.



C.

Figure 1. The unit cell of zeolite A.
A. The Gramlich and Meier conception
B. Dehydrated stereoview
c. Large dehydrated plotter picture

face a 16-member ring is formed consisting of 8 oxygen, 4 silicon, and 4 aluminum ions in the sequence . . .Al-O-Si-O-Al-O-Si. . .

Prior to 1972, nearly all of the knowledge of sorption and catalytic sites in zeolites was obtained through infrared spectroscopy,[18,19,20] NMR techniques,[21] and other spectroscopic methods. It was through these methods that bonding involving the sorbant molecules was first discussed.

In the 1960s the crystallographic study of stoichiometrically exchanged sorption complexes of zeolite A was initiated by Seff and Shoemaker.[22,23] Since that time many more workers have prepared variously ion-exchanged and complexed zeolites. Only a few of these have been investigated crystallographically.

D. The Objective of This Work

The immediate goal of this research is to prepare variously ion-exchanged zeolites, to experiment in complexing these with elements or small molecules, and to examine certain of these prepared novel complexes by the methods of X-ray crystallography.

II . X-RAY CRYSTALLOGRAPHY

A. Application To This Research

The ultimate objective of the research upon which this thesis is presented, is to provide a sub-microscopic basis for the understanding of the macroscopic physical and chemical properties of various cation exchanged or complexed zeolites. In particular, the determination of the Cartesian coordinates of the atoms in sorbed molecules and exchanged ions within the known, but somewhat flexible, zeolite framework, adds not only to the present understanding of the forces responsible for sorption and catalytic activity, but often lends insight into the chemistry of interaction between the exchanged and sorbed species. It is the unambiguous determination of the atomic positions within the unit cell of the variously ion-exchanged and complexed zeolite crystals which allows us to progress in our comprehension of these systems.

Many methods exist by which chemists are enabled to postulate structural molecular models. In many cases the employment of such methods as nuclear magnetic resonance, electron spin resonance, visible, infrared, ultraviolet, or microwave spectroscopy, is able to yield characteristic information about the investigated molecules, but in no case do these methods yield precise atomic positions in three-dimensional space.

Crystallography is the only technique capable of definitive molecular structure determination. The employment of X-ray crystallography commonly provides atomic resolutions greater than one hundredth of an angstrom, and consequently remains unparallelled by any non-diffraction technique.[24]

B. Historical Development

The intrique of crystalline materials has held the attention of naturlists for many centuries. The word crystal is derived from the Greek krystallos[25], which means, literally, frozen ice. The Greeks used this term for the mineral quartz, which they believed to be frozen water.

It is interesting that this belief was maintained until medieval times. As the science of mineralogy developed, the "frozen ice" hypothesis vanished and the study of many natural crystals strengthened the evidence which postulated that the external appearance of crystalline matter was indicative of internal order and composition.

Late in the seventeenth century the French abbot Rene' Just Haüy began to collect and investigate crystals as a hobby. Although Haüy began his scientific career relatively late - he was thirty - he soon became the foremost authority in the fields of crystal study and mineralogy. During the course of his investigations, Haüy once dropped, accidently, a crystal of calcite. He noted that all of the broken pieces resembled each other, and the larger crystal, in external shape. He continued to break the small pieces and found that section after section could be removed until all of the pieces were geometrically identical rhombohedra. Haüy's findings led to the concept of a crystal as a macroscopic sample of a solid substance composed of building blocks - atoms or molecules - which are orientated to each other in an orderly, symmetrical, periodic manner in three dimensions. Hauy is credited with over 100 crystallographic publications. His Treatise on Crystallography[26], a classic, was published in 1822, the year of his death.

X-rays were accidently discovered in 1895 by Wilhelm Conrad Roentgen,[27] who so named them because he was uncertain of their nature. These rays, which are also called roentgen rays, have since been found to constitute a portion of the

of the electromagnetic spectrum of radiation. X-rays are invisible, penetrating radiations, not unlike visible light in nature, but of a shorter wavelength (10^{-7} to 10^{-11} cm.). They are emitted from atoms due to spontaneous or artificially produced energy transitions within atomic electron shells. Experimentally, and comercially, X-rays are produced by bombarding a metallic target with a beam of high velocity electrons.

Max von Laue[28] of Germany, a copatriot of Roetgen, suggested in 1912 that crystalline solids might be employed as diffraction gratings for X-rays, since X-ray wavelengths are similiar to the intramolecular distances in crystals. If such a diffraction could be experimentally obtained, then crystallography could expand to include the quantitative study of internal crstalline order and establish precise molecular geometries. Laue's hypothesis was confirmed the same year by Friedrich and Knipping,[29] who were able to obtain diffraction patterns photographically. The successful structure determinations of NaCl and KCl in 1913 by W.C.Bragg,[30] the construction of the first X-ray spectrometer by Bragg's father, and the applicability of Bragg's Law, which predicts X-ray scattering, established X-ray crystallography as a science which has since become fundamental to molecular research.

C. Theory

Max von Laue formulated a unique, yet complicated, mathematical explaination of X-ray diffraction by crystals. However, it is W.C.Bragg's treatment of the phenomenon, in simple geometric terms, which has proved indespensible to an understanding of the diffraction concept.

Since the atoms or molecules, of which crystals are composed, are arranged in a three dimensional, orderly, periodic pattern, and since the distances between the atomic planes approximate the wavelengths of X-rays, crystals act as

three-dimensional gratings in their ability to diffract X-rays. The multi-dimensional diffraction which crystals produce is analogous to the diffraction of visible light by two dimensional gratings. Indeed, the younger Bragg once remarked that the principles of optical physics were prerequisite in the conception of his law.[31] Bragg's Law treats X-rays as if they are reflected by the atomic planes within a crystal. In his own words:

> "When a beam of monochromatic X-rays strikes a crystal, wavelets scattered by the atoms in each sheet combine to form a reflected wave. If the path difference for waves reflected by successive sheets is a whole number of wavelengths, the wave trains will combine to produce a strong reflected beam."(31)

Bragg's Law is the geometrical equation; $n\lambda = 2d \sin\theta$ (1)

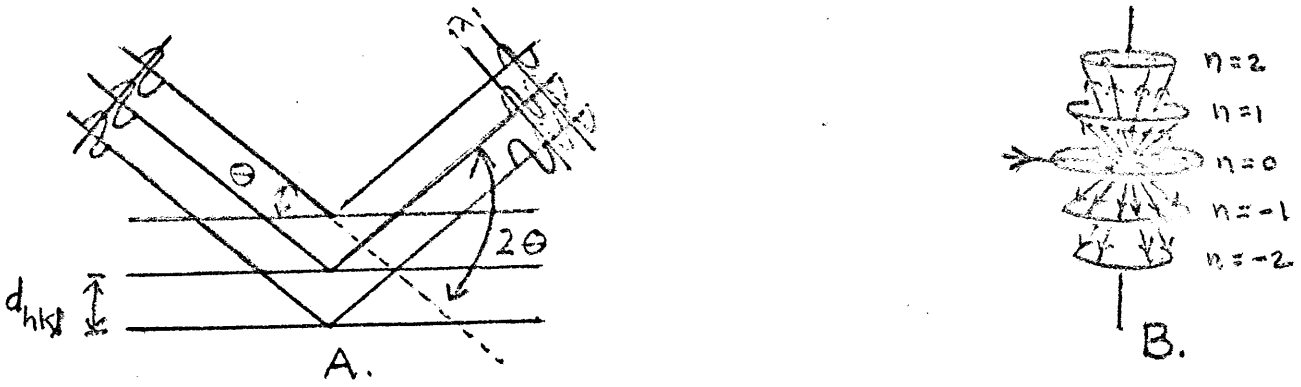


Figure 1. A. two dimensional diffraction. B. three dimensioal diffraction.

The perpendicular distance between reflecting planes is d_{hkl}, and θ is the glancing angle of the incident X-ray beam. The path difference of waves reflected by the planes is $2d \sin\theta$. Hence, there is only one angle θ, when λ and d_{hkl} are fixed, for which the reflected waves will be in phase. At any other angle there will be destructive interference and no reflection will be observed. There are a large number of atoms and these atoms may be of different types, consequently many different planes may be chosen, and for each layer of planes a different incident angle θ will be necessary to produce a reflection.

Successive planes are assigned Miller indices, h, k, ℓ, by which they are designated. These indices do not provide any physical measurement of the planes, but only define their orien tation in space. Several visualizations of such planes are presented in Figure 2.

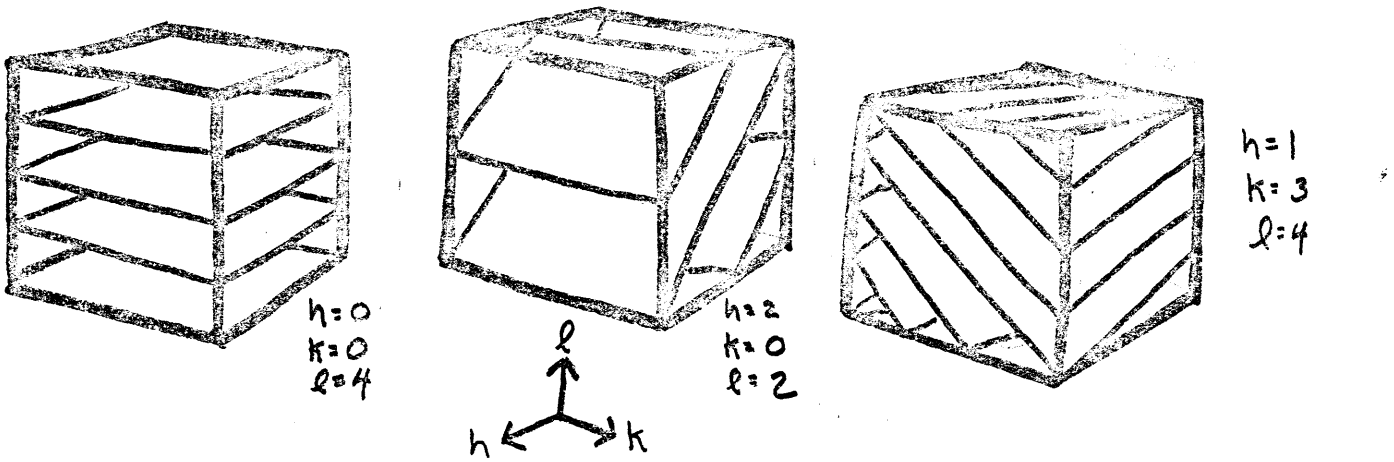


Figure 2. Atomic planes within a unit cell.

The intensity, $I_{hk\ell}$, of a diffracted wave and its phase - its time of arrival at the detecting device relative to other diffracted waves - is determined by the arrangement of the atoms within the unit cell (as opposed to the angle of reflection being determined by the distance between atomic planes of adjacent unit cells). The constructive-destructive interferences which exist within each set of diffracted waves also effects the observed intensities. Theoretically, the solution to any crystal structure may be achieved from angle, intensity and phase of the reflected beam. Unfortunately, it is impossible to measure the phase of the diffracted radiation by any means. At present, film and scintillation detectors are utilized in recording the angle and intensity information of the diffracted beam. These are "square law" detectors and hence $I_{hk\ell}$, which includes both the amplitude and phase of the beam, cannot be directly established. Nevertheless, we can obtain through these detectors a complex factor, $F_{hk\ell}$, which can be related to the diffraction intensity; $I_{hk\ell} \propto F_{hk\ell}^2$. $F_{hk\ell}$ is called the structure factor. The phase

of the reflection is lost when $I_{hk\ell}$ is squared. Hence, beyond our determination, any diffracted wave may be from 0° to 180° out of phase with any other. In X-ray crystallography this uncertainty is known as the phase problem, and is the most formidable obstacle in any structure determination.

In consideration of all that has been mentioned, there exist a function which relates the obtainable data of diffraction with the electron density (ρ) at any atomic position x, y, z within the unit cell. It is;

$$\rho(x,y,z) = \frac{1}{V} \sum_{h}^{+\infty} \sum_{k}^{+\infty} \sum_{\ell}^{+\infty} \left[F_{hk} \exp(-2\pi i(hx+ky+\ell z)) \right] \qquad (11)$$

The yet unexplained components are V, which is the unit cell volume, and i, which is simply $\sqrt{-1}$. The atomic positions of the crystallized molecules under investigation may be attained thru function(11) by the crystallographer, aided by the employment of the equipment and methods described in the remainder of this chapter.

D. Equipment And Methods

The Bragg X-ray spectrometer, used with an ionization chamber, was the first device utilized to collect data on the intensity of X-ray reflections. The development of X-ray photographic films soon replaced this method. In fact, until the last decade, intensity data was collected almost entirely by film methods.

These methods were never especially precise since the recorded intensities usually had to be measured visually. Processing of the films, scaling the data and camera maintenance were tedious and time consuming chores. The percentage of accuracy which was lost through the equipment and human error rarely allowed reliable determination of thermal motion or precise bond lengths. Nevertheless, the multitude and importance of the structures which were correctly determined by these methods remains a tribute to the crystallographers working in the first

half of this century.

In the 1950s the development of automated diffractometers led to what one author called a " revolution in crystallography".[32] These diffractometers mimiced the geometry of the traditional photographic data collection systems, but otherwise had little in common. The angles at which reflections might be found were calculated by modular computers. Angular settings were reached by highly synchronous motors. Intensity collection was accomplished using sensitive scintillation counters, similiar to Geiger counters. Data recording was on paper tapes, punched cards, or magnetic tapes which could be directly processed into a computer for further work in strucutre determination. The auto-diffractometers have decreased human error and increased experimental accuracy and precision. Most significantly, they have contributed to the application of crystallography in many fields which hitherto did not have the time or staff to invest in crystallographic investigations.

A Syntex $P\bar{1}$ four-circle, computer-controlled automated diffractometer (hereafter referred to as the $P\bar{1}$) with graphite-monochromatized Mo radiation was used for preliminary experiments and for the collection of diffraction intensities for the structure determinations to be discussed shortly. Diffractometer computer input instruction is achieved in the P1 by teletype, paper tape, or magnetic tape. Output data utilizes these same mediums. A pulse height analyizer and a strip chart recorder are also modular components of the $P\bar{1}$. The $P\bar{1}$ modular computer is a Data General Corporation NOVA, which has a 4096, 16-bit word, core storage, and in a typical structure investigation executes the necessary programs for automated crystal set up and data collection. The first of these programs is Centering & Auto-Indexing, which centers up to fifteen reflections and determines indices for these, after being supplied starting input from initial Polaroid film coordinates. A Least Squares Or-

ientation Matrix program determines unit cell parameters from indices and 2θ data and calculates angles from an orientation matrix and indices. The Automatic Data Collection program provides a fixed or variable scan mode of operation, records crystal X-ray exposure time, list Miller indices in any order desired, provides a means of limiting output data recorded, and prints out the peaks, intensities, deviations and angles of all observed reflections. A descriptive picture of the $\overline{P1}$ and a sample of its printed output may be found in Appendix A.

The methods of processing the output data from the P1 rely on the accessibility of high speed, high capacity digital computers. Fortunately, this University has available an IBM360/65, which is capable of handling the volume and complexity of the programs which are routinely used in most X-ray crystallographic structure studies.

Because they have been essential to the solution (or attempted solution) of the structures with which this thesis is concerned, and because an explaination of them concomittantly explains the method of solution, the computer programs employed after data collection are here briefly described. Samples of their outputs may be found in Appendix B.

LPCOR[33] is a Fortran computer program designed to process the P1 output tape. It selects significant reflections (those which have an intensity greater than three times there standard deviation) and applies crystal absorption or decay correction curves to these reflections if necessary. LPCOR outputs punched IBM cards containing significant reflection indices, the reflected intensities, and deviations.

PACKEM[34] is a simple Fortran program which condenses the output from LPCOR by placing three reflections on each IBM card.

FMLS[35] is a Fortran program which provides full-matrix least-squares refinement of suitable trial crystal structures. It refines atomic positional and thermal parameters in an attempt to match the calculated structure factors with those observed. FMLS also calculates the error index, R, ($R=(\Sigma||F_o|-|F_c||)/\Sigma F_o$) which is indicative of the fit between the structure factors calculated from the trial structure, and the observed structure factors.

SFC-ALFF[36] is a PL/1 program which performs Fourier summations. This program produces an electron density map from significant data. This map contains peaks which may correspond to unfound atomic positions. These positions can then be added to future trial structures.

MGEOM[37] is a Fortran program which calculates all intramolecular bonding distances and angles from input postulated or known Cartesian coordinate positions within the structural model.

ORTEP[38] is a Fortran program which, when supplied the final three-coordinate atomic positions within a unit cell, draws on a computer plotter, two pictures of the molecule whose structure has been determined. These pictures are drawn with a 6° difference in rotation. Viewed thru stereoglasses, these pictures appear as one three-dimensional molecule, and allow the molecule to be "seen"

III. EXPERIMENTAL PREPARATIONS

A. Zeolite Synthesis

The original synthetic production of zeolites in the late 1950's was an important breakthrough because it made available quantities of zeolite which were impractical or impossible to obtain from nature. However, these synthetics were either amorphous or microcrystalline, and this limited the studies which could be carried out on them. Precise determination of atomic positions by X-ray diffraction requires single crystals approximately 150μm or larger in diameter for optimum results[39]. Comercially synthesised crystals range from 1 to 10μm and are thus unsuitable for this purpose[40]. In 1967 a method of preparing crystals of zeolite A, with a maximum diameter of 100μm was published[41]. By 1970 Charnell[42] had prepared crystals approaching 140μm in diameter, and the crystals used in this research were consequently prepared by his method, with a modification to include a second crystallization using seed crystals from the first preparation. These crystals are grown from a hydrothermal gel by reacting sodium metasilicate with sodium aluminate, using triethanolamine as a stabilizing and buffering agent. The consistency of the crystallization yield and quality varies with temperature, reagents, and procedure used in the preparation. An available supply of adequate zeolite A crystals permitted this work to proceed with the ion-exchange experiments and sorption work.

The sources for all chemicals utilized may be found in Appendix . All of the analysis' were performed at Galbraith Laboratories, in Knoxville,Tennessee.

B. Ion-Exchange

For the following exchanges, carried out at room temperature, a ten-fold excess of the exchanging ion with respect to the ion to be exchanged was used.

Calcium

50ml. of 0.1M calcium nitrate, $Ca(NO_3)_2 \cdot 4H_2O$, was placed in a flask with 0.5 grams of zeolite A. The solution was gently stirred and the zeolite sample was microscopically observed, daily, for a week. The appearance of the crystals remained unchanged during this period. On the seventh day the crystals were filtered from solution, washed four times with distilled H_2O, and allowed to dry. An analysis indicated that the sample contained 3.60% calcium by weight. This corresponds to 2.01 Ca^{++} per unit cell, substantially less than would be expected in a complete exchange.

Zinc

100ml. of 0.1M zinc nitrate, $Zn(NO_3)_2 \cdot XH_2O$, was placed in a flask with 1.0 gram of zeolite A. The solution was stirred and the zeolite sample was examined, by microscope, daily for a week. On the third day the crystals, which were initially very clear, had become somewhat cloudy. No further change was noted and, on the seventh day, they were filtered from solution, washed four times with distilled H_2O, and allowed to dry. An analysis indicated that the sample contained 14.67% zinc by weight. This corresponds to 5.23 Zn^{++} per unit cell, almost a total exchange. Subsequent crystallographic study[43] of these crystals confirmed this analysis.

Manganese

Preliminary experiments using Linde Zeolite A powder and $Mn(ClO_4)_2 \cdot 4H_2O$ in-

dicated, by a fast color change(in two hours) of the white powder to dullish pink-brown, that an attempted Mn exchange might be feasible. Accordingly, 50ml. of 0.1M $Mn(ClO_4)_2 \cdot 4H2O$ was placed in a flask with 0.5 grams of zeolite A. Within two hours the crystals appeared pink to the unaided eye but, with the exception of their slight dullness, appeared no different than untreated zeolite A crystals under the microscope. On the second day of exchange the sample appeared brown, but under the microscope they looked redish-pink. No further changes were noted during the exchange period. On the seventh day the crystals were filtered from solution, washed four times with distilled H_2O, and allowed to dry. An analysis indicated that the sample contained 10.68% Mn by weight. This corresponds to 4.41 Mn^{++} per unit cell.

A second Mn exchange was performed. It was carried out exactly as the first, except that the crystals were not harvested for five months. There was no change in crystal appearance after the third day. The solution was stirred daily for the first week, and weekly for the duration of the exchange. At the end of five months the crystals were filtered from solution, washed four times with distilled H_2O, and allowed to dry. An analysis indicated 10.97% Mn by weight. This corresponds to 4.53 Mn^{++} per unit cell, an increase of only 0.12 Mn^{++} after the much longer exchange. Subsequent crystallographic study confirmed this analysis. The structure determination of several complexes of crystals from this batch has been completed [44,45,46].

Cobalt

50ml. of 0.05M cobalt nitrate, $Co(NO_3)_2 \cdot XH_2O$, was placed in a flask with 0.6 grams of zeolite A. The solution was gently stirred and zeolite samples were observed daily by microscope, for a week. The crystals appeared pink by the end of a week. They were allowed to exchange for a month, at the end of which they were filtered from solution, washed four times with distilled H_2O,

and allowed to dry. It is interesting that this zeolite sample, which contained larger crystals than had previously been used in cobalt exchange[47], retained a pink color, as opposed to the other cobalt zeolite complexes, which have been brown. Crystallographic studies presently being carried out on these crystals indicate 4.0 Co^{++} per unit cell of zeolite[48,49].

Iron

50ml. of 0.5M ferous sulfate, $FeSO_4 \cdot 7H_2O$, was placed in a flask with 0.5 grams of zeolite A. After one day the zeolite and solution became a rust rust color. The zeolite appeared to be destroyed. Because no measure of success had previously been attained in Fe^{++} exchange[50], this exchange was not pursued, so that more productive work could be continued.

Gold

100ml. of 0.002M gold cloride, $AuCl_3 \cdot HCl \cdot 3H_2O$, was placed in a flask with o.5 grams of zeolite A. The solution was freshened every day for three days. Although most crystals initially became pale yellow, some turned purple, and the gold soultion became purple, by the end of a week. This color, called Purple of Cassius[51] is indicative of finely divided gold, suggesting that other processes were taking place besides ionic exchange. At the time of this writing, gold exchange is still being investigated. It has been observed that although aggregates of the crystals appear purple, single crystals in solution are yellow-gold.

Previous work has investigated the exchange of other ionic species into the zeolite[52,53]. This work has shown that some cations destroy the zeolite framework, making the exchange worthless. To remedy this, a solution flow apparatus using low cation solution concentrations was employed (see figure 4). The flow of solution passing through the zeolite, contained in a 25ml. sintered

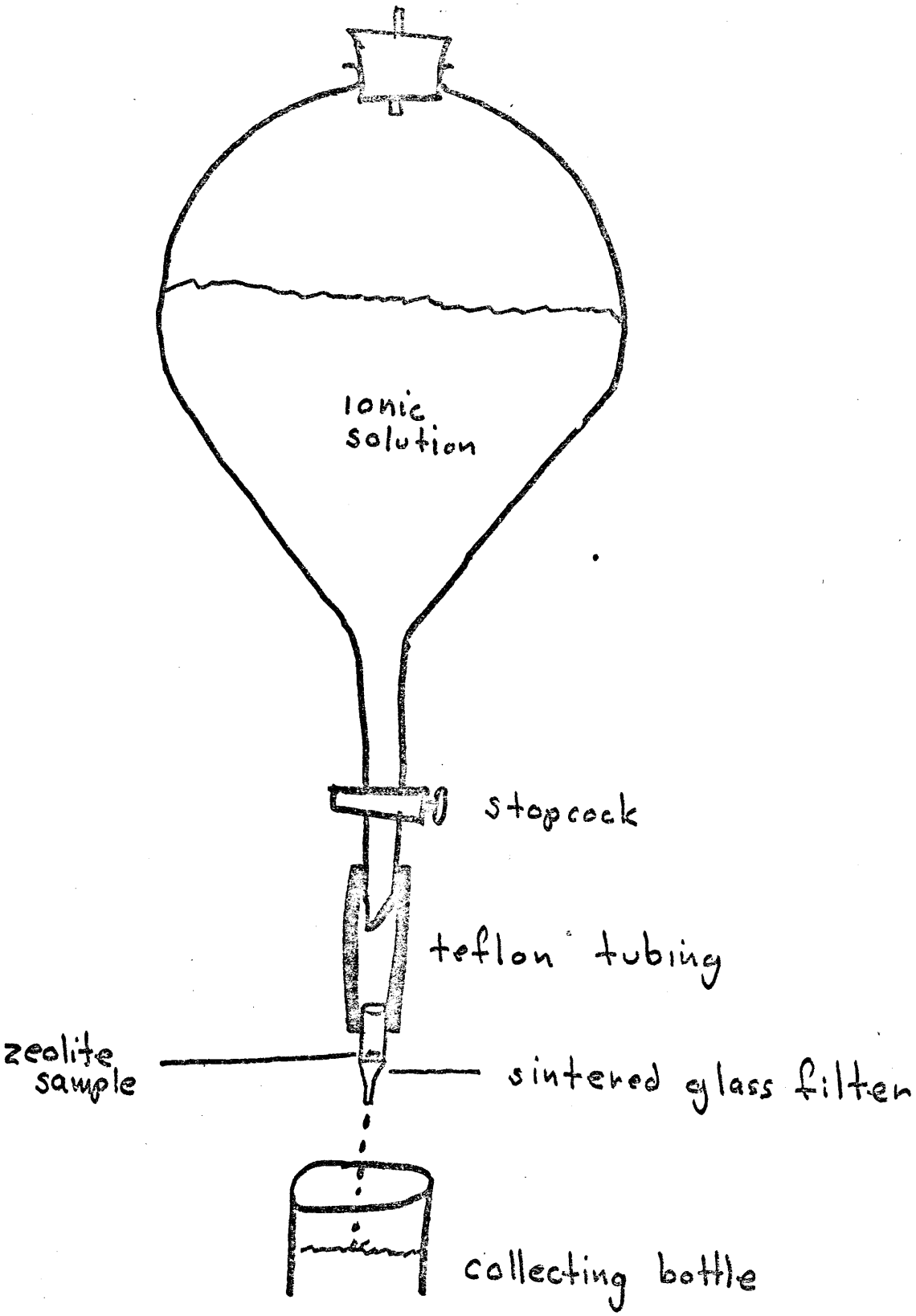


Figure 4. Solution flow apparatus.

filter, could be controlled by a stopcock. A fresh solution could be continually in contact with the zeolite sample, preventing the exchanged ions from remaining in solution and hindering equilibrium. Experimentation using progressively lower concentrations of solutions proved to be helpful in preserving the zeolite structure (by visual inspection).

The following exchanges were performed using this technique.

Copper

Four liters of 0.001 cupric nitrate, $Cu(NO3)_2 \cdot 3H_2O$, were allowed to flow through the filter containing 0.5 grams of zeolite A. The zeolite was then removed from the apparatus, washed four times with distilled H_2O, and allowed to dry. An analysis indicated 5.52% Cu by weight. This corresponds to approximately 2 Cu^{++} per unit cell. This is far from the maximum possible exchange, and work is currently in progress to achieve a more complete exchange. It is significant, however, that the zeolite sample was in no way destroyed.

Silver

Five liters of 0.005M silver nitrate, $AgNO_3$, were allowed to flow through the filter containing 0.5 grams of zeolite A. The zeolite was then removed from the apparatus, washed four times with distilled H_2O, and allowed to dry. The crystals were dark, and after exposure to room temperature, atmosphere and the distilled H_2O, the crystals became black. It is possible that this was the result of some photochemical effect. No analysis was obtained, and there is presently more work with lower concentrations of silver nitrate solution being completed.

Chromium

Four liters of 0.005M chromic nitrate, $Cr(NO_3)_3 \cdot 9H_2O$, were allowed to flow through the filter containing 0.5 grams of zeolite A. The zeolite sample was then removed from the apparatus, washed four times with distilled H_2O, and

allowed to dry. The crystals appeared to be destroyed. They were green-blue in color. Work at lower concentrations is being continued.

C.Sorption

1) elemental

Elemental sorption experiments were carried out using selenium and tellurium. These elements were chosen because they are not only of some biological importance[54], but as semimetallic elements, are known to exhibit a range of unusual electrical properties. Selenium is photovoltaic and photoconductive. It is used in photo cells, exposure meters, solar cells and rectifiers. Tellurium possesses many of the same properties of selenium. These elements have found use in many electronic and solid state applications, including xerography. Previous work has been undertaken with tellurium loaded zeolites[55], , but this study did not employ zeolite A. The sorption of sulfur into zeolite A and the crystallographic study of the complex has also been completed[56]. Because selenium and tellurium are also Group VI elements, it could be expected that there zeolite A complexes might offer interesting comparisons and perhaps similiarly unique characteristics.

Selenium

The adsorption of selenium onto zeolite A, calcium exchanged zeolite A (referred to as zeolite 5A), and cobalt exchanged zeolite A (referred to as that), was performed simultaneously. Approximately 50 mg. of the particular zeolite sample was placed in a glass tube, 12 mm in diameter. A calculated amount of selenium powder, cprresponding to 24 atoms per unit cell of zeolite, was placed in the glass tubes. The individual tubes were marked for high- temperature identification. The tubes containing the samples were then attached to a vacuum system equipped with a Mercury diffusion pump, and a low-temperature gas trap. A

small oven was then fitted over the samples. Figure 5 illustrates the configuration. Unfortunately, the system was not equipped with a McLeod guage to measure the vacuum precisely. After the system's iol vacuum pump was operating for six hours, the Mercury pump was turned on. From the start, the oven temperature was allowed to gradually increase over a twentyfour hour period, until 350°C was reached. The samples were kept at this temperature, with not more than a 15° variation, for another twentyfour hours. It was hoped that this procedure would permit dehydration of the zeolite and sorption of the selenium.

It was noted prior to the end of the final twentyfour hour period, that the insides of the tubes above the top of the oven, had accumulated gray and orange deposits. These colors are characteristic of selenium in the amorphous state, indicating that, as expected, the selenium vaporized at the oven temperature and solidified upon cooling as it vaporized past the oven.

When the vacuum system was shut down and the oven taken off, it was observed that the system's low temperature gas trap was slightly glazed with shiny balck and silvery red deposits. This indicated that more selenium, in the gasous state, had left the sample tubes in addition to that previously noted. At this time the possibility that enough selenium was lost so as not to achieve maximum sorption, was contemplated. The samples were sealed off from the vacuum line using a natural-gas-oxygen torch. The vacuum was not lost.

The following observations were made of the samples in the sealed off vials.

selenium-zeolite A sample;

appeared to the unaided eye, to be white in color, and under the microscope looked to be empty zeolite A.

selenium-zeolite 5A;

to the eye was dark yellow, and under the microscope the crystals looked candy yellow. They maintained their crystallinity and did not in any way seem adversely affected by the sorption procedure.

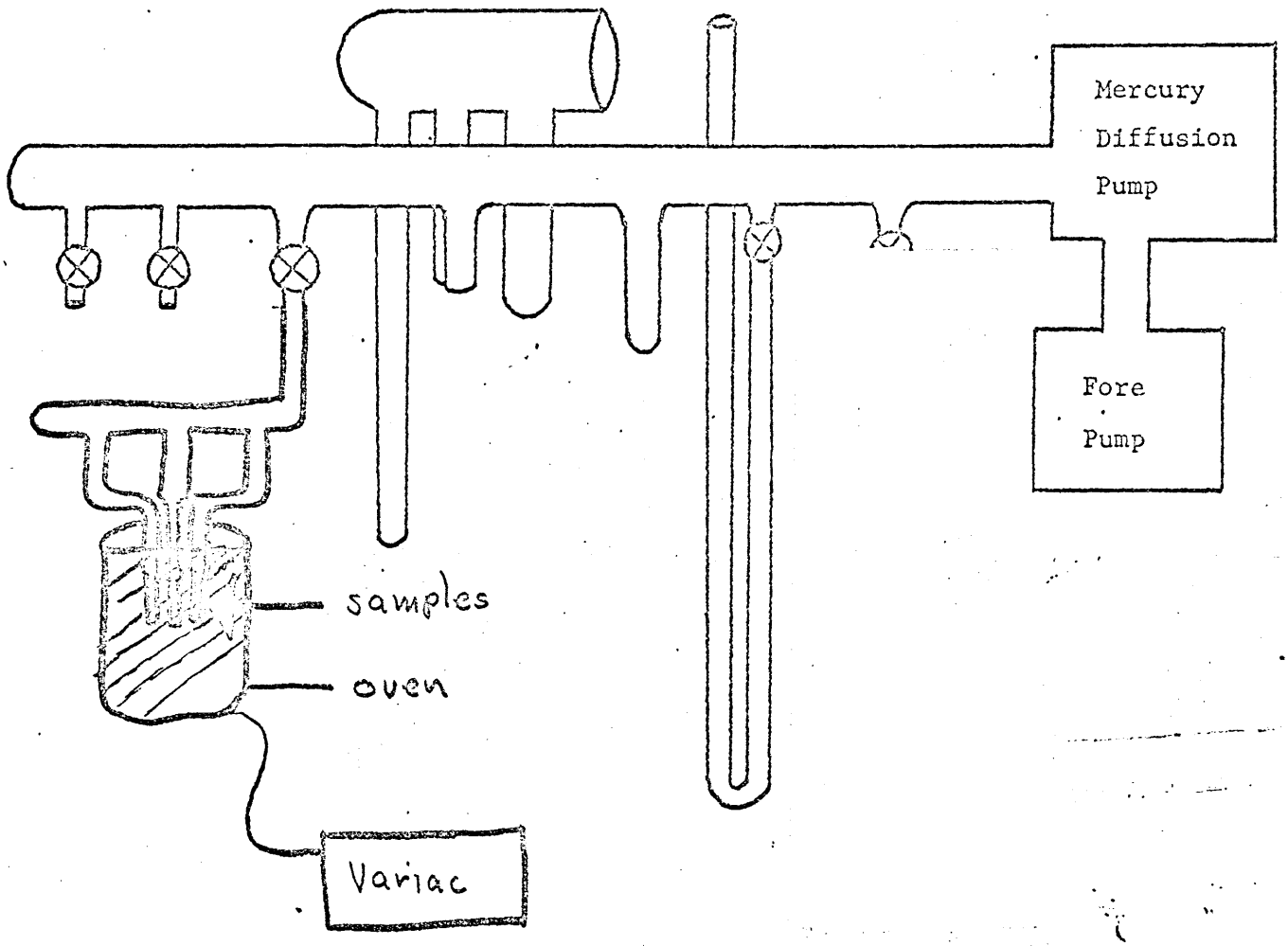


Figure 5. Dehydration - sorption vacuum system

selenium- cobalt exchanged zeolite A;

looked dark blue-black to the unaided eye. Under ,the microscope the crystals looked like charcoal with small blue pepples thrown about. The The vial containing this sample was accidently dropped, and it's investigation was at this point terminated. From the information recorded, it is postulated that the cobalt exchanged crystals were destroyed.

After these observations were made the sample vials of selenium zeolite A and selenium zeolite 5A were placed in a muffle furnance. The temperature was again increased to 350°C over a twentyfour hour period. After two additional days at this temperature, the vials were removed and the following observations were made.

selenium - zeolite A sample;

initially tan upon removal from the oven, becoming light yellow after a few minutes upon cooling.

selenium - zeolite 5A;

initially iron red upon removal from the oven, becoming dark orange upon cooling.

The color changes of both samples suggested that more selenium entered the zeolite than had under the previous conditions. The color change thus suggested that more selenium could be sorpted.

The selenium-zeolite A vial contained a surplus of selenium, but little selenium remained in the selenium-zeolite 5A vial. Accordingly, the later was broken open, and the contents plus 70 mg. of additional selenium were placed in a new, modified glass tube (figure 6). The modification consisted of an expansion in the upper portion of the tube to allow a condensation of selenium vapor. Prior to seal off, the deposits in this area could be moved back into the vial by heat treatment with the torch. This sample was then

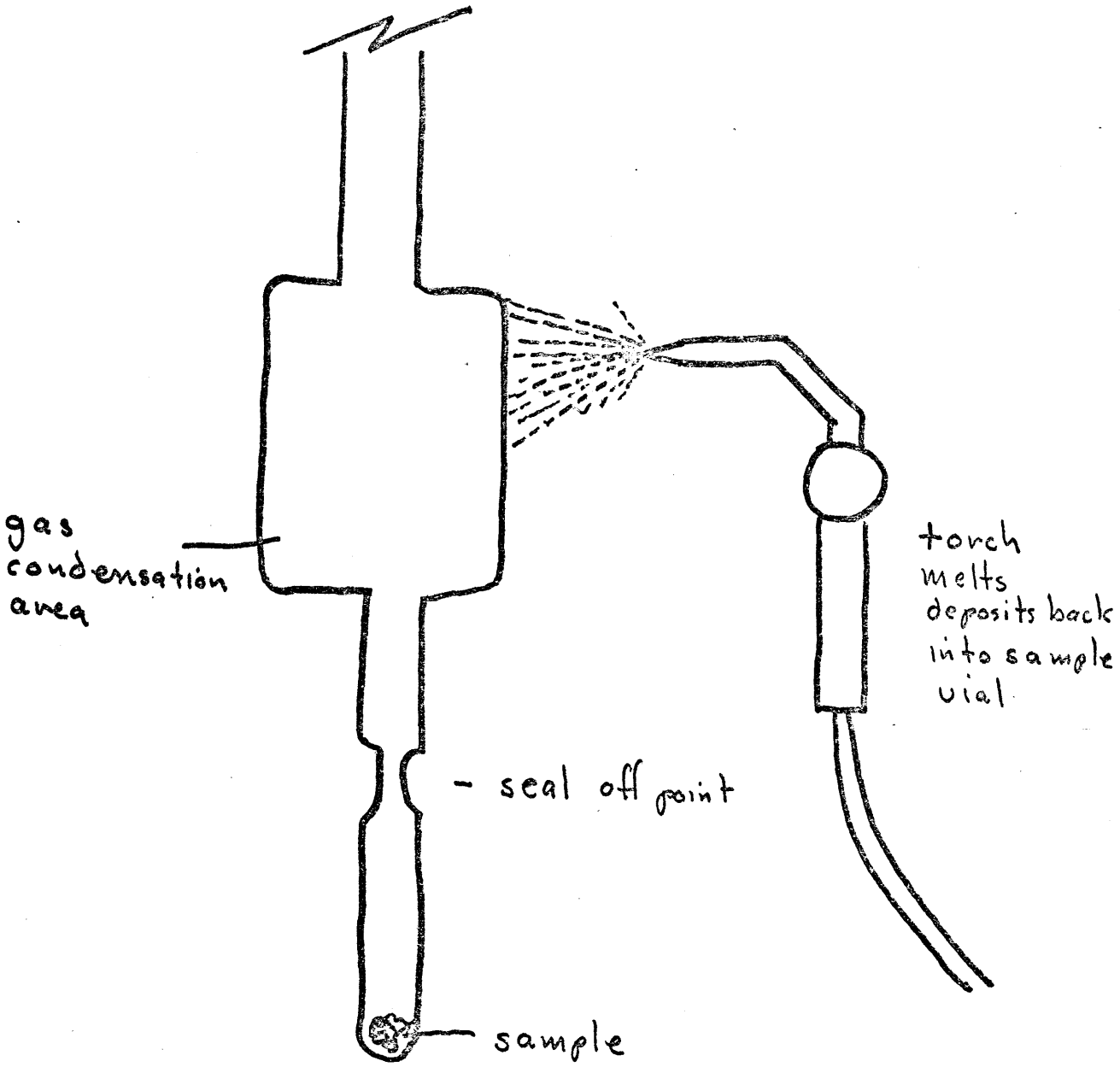


Figure 7. Modified sample containing tube.

attached to the vacuum line and the dehydration - sorption procedure was followed as before.

The vial was sealed off, after the three day period, and it was observed that the contents were now dark yellow-orange.

Both the selenium-zeolite A and the selenium-zeolite 5A vials were now placed in the muffle furnance for seven days at 350°C. The variac used to control oven temperature misfunctioned during one twelve hour period, and the temperature rose to 600°C. The samples did not appear adversely affected by this (zeolite A is stable to 750°C).

After this final interval in the furnance, the following observations were made.

selenium-zeolite A sample;

red-brown out of the furnance, changing to yellow-orange upon cooling. Some selenium remains in the vial. There is no further color change when the vial is broken open.

selenium-zeolite 5A sample;

red-orange out of the oven, changing to brilliant orange upon cooling. Some selenium remains in the vial. There is no further color change when the vial is broken open. An analysis indicated 8.84 selenium atoms per unit cell of the zeolite. Crystallographic investigation of this sample is discissed in the next chapter.

Tellurium

The adsorption of tellurium onto zeolite A, zeolite 5A, and cobalt exchanged zeolite A, was performed simultaneously. Approximately 50 mg. of the particular zeolite sample was placed in individual glass tubes, 12 mm in diameter. A calculated amount of tellurium powder, corresponding to twentyfour atoms per unit cell of zeolite, was also placed in each tube. The tubes were marked for ident-

ification as before. They were also modified for gas condensation, and then attached to the vacuum system already described. Within six hours the vacuum was complete, and the temperature of the oven fitted over the samples was gradually increased to 350℃, over a twentyfour hour period. The temperature remained at 350℃, with not more than a 10° variation, for another full day. At that time the samples were sealed off from the vacuum line. The vacuum was not lost.

The following observations were recorded.

tellurium-zeolite A sample; no change in color or appearence

tellurium-zeolite 5A sample; no change in color or appearence

tellurium-cobalt exchanged zeolite A; sample appears black and destroyed

The vials were then placed in the muffle furnance, and the temperature was gradually brought to 550°C and left at this temperature for a week. At the end of the week the samples were removed, and the vials were broken open. The following observation were recorded.

tellurium-zeolite A sample;

this sample contains some silvery tellurium deposits, but there is a lot of white material which looks like melted mothballs. There are no single crystals. Apparently, the zeolite was destroyed.

tellurium-zeolite 5A sample;

this sample also contains some silvery tellurium,some crystals are brown, some are black. It cannot be determined in the zeolitic structure has been destroyed.

tellurium-cobalt exchanged zeolite A sample;

there exist many single crystals in this sample, but they are all black.

No analytical or crystallographic study of these samples has been initiated, due to the low tellurium occupancies anticipated; this problem promised to be more bothersome for these samples than it was in the similiarly prepared selenium cry-

stals.

2) molecular sorption

Zinc exchanged zeolite A was chosen for experimentation in acetylene sorption. Some work had already shown that hydrocarbon-zeolite complexes could be successfully prepared and crystallographically studied[57,]. Because this would be a gasous sorption, a single crystal of the prepared complex, 75μm on an edge, was selected and placed carefully in a small, 100μm, glass capillary. The capillary was then sealed onto a vacuum system equipped with a zeolite buffer system to insure that the acetylene vapor exposed to the crystal would be entirely dry. The system was also equipped with a McLeod guage, so that the vacuum could be measured accurately. In order to dehydrate the crystal, an oven was fitted over the capillary and the temperature elevated to 350°C at a pressure of approximately 1×10^{-6} torr for fourtyeight hours. The crystal was then exposed to 650 torr of 99.6% pure acetylene for twentyfour hours. Amaro's work with unexchanged zeolite A, indicated that this would be sifficient to introduce about six molecules of acetylene into each unit cell of the crystal. After reaching equilibrium the crystal in the capillary was carefully sealed off the vacuum system. A diagram of the vacuum system set up is presented in figure 7.

It is known that zinc exchanged zeolites are very hydrophilic. This was firmly established for zeolite A after this author completed the crystallographic study of the zinc complex presented here. Although no acetylene entered the zeolite, this work did permit recognition of the hydrophilic nature of the complex, and further was able to yield a valid structure determination of the hydrated zinc-zeolite complex.

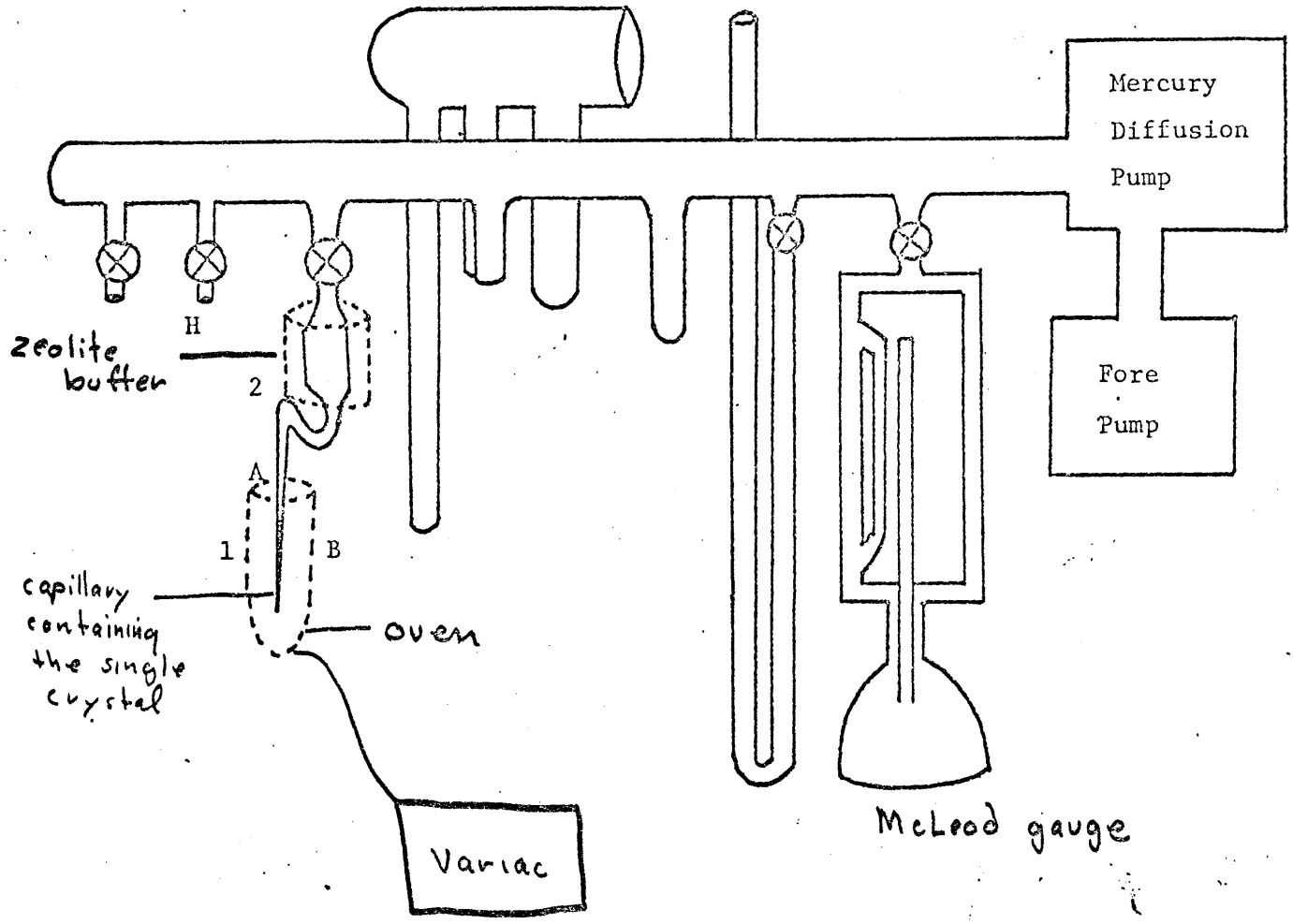


Figure 7. Single crystal vacuum system.

IV. EXPERIMENTAL CRYSTALLOGRAPHIC METHODS USED IN THE STRUCTURE DETERMINATION OF $Se_8Ca_2Na_8(A)\cdot XH_2O$ and $Zn_5Na_2(A)\cdot 29H_2O$

The ion-exchange and complexation of $Se_8Ca_2Na_8(A)\cdot XH_2O$, referred to in the furture as (I), and $Zn_5Na_2(A)\cdot 29H_2O$, referred to in the future as (II), has been described in chapter VI.

A single crystal of (I), 75μ on an edge, was placed on a glass needle. This and the capillary containing the single crystal of (II) were each mounted on a Stoe goniometer head of a type designed to make adjustments in the x, y, and z directions. For each data set, a Syntex four-circle computer-controlled diffractometer with graphite-monochromatized Mo $K\alpha$ radiation was used throughout for preliminary experiments and for the collection of diffraction intensities. The data sets were collected at approximately the same temperature (20°C) and humidity. The temperature range during any one data collection never varied more than 0.5°.

Both structures have been refined in the same space group $Pm\bar{3}m$ rather than $Fm\bar{3}c$, because of the suspected absence of long range order in the silicon and aluminum positions. Due to the possible excess of silicon to aluminum, as indicated by elemental analysis, an occasional silicon-oxygen-silicon bond is probably present in some unit cells which strictly prohibits refinement in $Fm\bar{3}c$. A check of Gramlich and Meier's[58] most intense "b" reflections (which could be present in the $Fm\bar{3}c$ space group) were found to be absent in materials from the same crystallizations[59,60,61] as those used in this work. Gramlich and Meier[58] have shown that, even when appropriate, framework deviations are small. Therefore, in structure refinement, no distinction was made between silicon and aluminum atoms; they were refined at one equipoint and were considered as one

luminum atoms; they were refined at one equipoint and were considered as one type of atom.

No reciprocal lattice points were examined above the 2θ value of 70° because previous data sets have indicated very few reflections of significant intensity in this range. For each data set the θ-2θ scan technique was employed at a constant scan rate of 0.5°/ minute (in 2θ). The scan range was varied between 2.0° at 2θ = 3° to 2.5° at 2θ = 70°. A time equal to half the scan time was spent counting background at each end of the scan range.

Standard deviations on the net counts sampled at each point in reciprocal space were assigned according to the formula:

$$\sigma(I) = [CT + 0.25\,(t_c/t_b)^2\,(B_1+B_2) + (pI)^2]^{1/2}$$

where CT is the total integrated count obtained in time t_c, B_1 and B_2 are the background counts each obtained in time t_b, and $I = CT - 0.5(t_c/t_b)(B_1 + B_2)$. To account for instrument instability, a value of 0.02 was assigned to the emperical parameter p. The intensity and standard deviation for each reflection was corrected for Lorentz and polarization effects. A reflection was determined tc be significant, and therefore included in least-squares structure refinements, if its intensity exceeded three times its standard deviation.

Each structure was refined by a combination of full-matrix least-squares methods and three-dimensional electron density Fourier maps using phases determined in the previous least-squares refinement.

The two error functions used as criteria for suitable least-squares refinement are $R_1 = (\Sigma\,||F_o| - |F_c||)/\Sigma F_o$ and the generalized weighted index, $R_2 = (\Sigma\omega(F_o - |F_c|)^2 / \Sigma\omega F_o^{\,2})^{1/2}$. In general, a lower set of error functions indicates the possibility of suitable refinement of the atomic positions in question. However, other factors are considered - the equipoint in question must also refine to physically reasonable positional and thermal parameters. Because a thermal parameter is sensitive to the occupancy of the equipoint, the occupancy can be largely determined by requiring that the corresponding thermal parameter

can be largely determined by requiring that the corresponding thermal parameter be reasonable. Another indicator is the goodness-of-fit, $(\Sigma w(F_o-F_c)^2/(m-s))^{1/2}$, where F_o and F_c have the previously defined values, m is the number of observations, and s is the total number of individually varying parameters. The goodness-of-fit indicates the suitability of the weighting scheme; its ideal value at the conclusion of structure determination is 1.0.

Possible atomic positions are obtained from peaks on Fourier electron density maps in which the contributions of the framework and of some cations have been subtracted out, and Fourier electron density maps in which all atoms in the structure are displayed. For such small data sets as are commonly obtained for these zeolite structures (less than 250 observations), occasional erroneous peaks can be expected. Because the atoms we wish to locate usually have only moderate scattering factors, generally have higher thermal parameters, suffer from the effects of disorder, and have small occupancy parameters, their peaks on the Fourier maps are not expected to be large. Therefore, it is crucial that acceptable refinement, when and if it occurs, successfully describe previously unlocated atoms. Such refinement has proved successful[59]. All peaks above the 3σ level were tested in least-squares.

The form factor tables needed for Si^{++}, $AL^{+1.5}$, O^{-1}, Zn^{++}, Se, Ca^{++}, and Na^{+} were taken directly from the International Tables for X-Ray Crystallography[61] or interpolated where necessary. The charges assigned to the ions were generally taken to be half of their formal charges, to account for partial covalent bonding. The Zn^{++} form factor was corrected[62] for the effects of anomalous dispersion.

IV. THE ATTEMPTED DETERMINATION OF THE STRUCTURE OF $Se_8Ca_2Na_8(A)\cdot XH_2O$

A. Structure Refinement

The output of the LPCOR computer program indicated that of 876 reflections, 99 were significant.

Initial full-matrix least-squares refinement based upon the refined framework positions of the sulfur complex of zeolite A[56] converged, in six cycles, to an R_1 index of 0.211 and an R_2 index of 0.175. A sodium ion position at .15,.15, .15, was allowed to refine anistropically in these refinements. (The tables at the end of this section give the coordinates of all models discussed.)

An initial Fourier electron density map based upon the refined positions produced 10 peaks in the intensity range to $e^-/\mathring{A}^3$: the estimated standard deviation of the electron density was $e^-/\mathring{A}^3$. The strongest peaks found from the map, at .22, .22, .22, and .23, .5, .5, were included with the previously refined positions in four cycles of refinement as four sodium and four selenium atoms respectively. Although these new positions refined relatively well, the anisotropic sodium thermal parameter refined to physically unrealistic values, and R_1 rose to 0.25, and R_2 rose to 0.23.

The anisotropic sodium position was removed. A calcium position at 0.0, .34,.34, and a second selenium position at .25, .25, .5, were added. After four cycles these positions converged to an R_1 of 0.198 and an R_2 of 0.18. The isotropic thermal parameters for calcium and Se(2) rose, from 3.0 to 30.4 and 34.2 respectively. Se(2),(here on called Se(1)) was allowed to refine off the three-fold axis for four cycles, but its thermal parameter went down only slightly (26.4) and R_1 and R_2 both increased, to 0.21 and 0.19 respectively.

Four more cycles of least-squares were run, with only the framework and the stable calcium and selenium positions, prior to executing a second Fourier map. These positions remained stable. Several cycles also included another selenium position (occupancy of four) at .32, .32, .32, but its thermal parameter diverged upwards. Hence a second Fourier three-dimensional electron density map was produced based on only the framework and the stable calcium and selenium positions. The map contained 14 peaks in the intensity range from to $e^-/\AA^3$; the estimated standard deviation of the electron density was $e^-/\AA^3$. The peaks from this and the initial map are listed in Table 1.

Analysis of this map guided the input of four selenium atoms at .34, .34, .34, and four sodium ions at .24, .5, .5. Four cycles of least-squares converged to an R_1 of 0.24 and an R_2 of 0.21. Thermal parameters remained stable except for that of O(2), which rose from 3.3 to 14.25, and the added selenium, which rose to 44.0 . In an attempt to remedy this high thermal parameter, Se(2) was taken off the three-fold axis for further refinement. This, howeverm caused only a slight decrease in the Se(2) thermal parameter, and increased the Se(1) thermal parameter to 25.2. R_1 and R_2 were now at 0.199 and 0.184 respectively.

Se(2) was then placed back on the three-fold axis, in a slightly different position, but agin did not refine well.

At this point the calcium position was allowed to refine anisotropically. The thermal parameters for both selenium positions rose to about 30.0, and R_1 and R_2 decreased slightly to 0.19 and 0.16 respectively. After one more cycle of refinement, however, the selenium thermal parameters rose to about 40.0. R_1 and R_2 rose significantly.

Two more positions found from the second Fourier map were assigned as H_2O positions, although they had initially thought to have been background noise. After four cycles, their thermal parameters became negative. They were

then reset, with occupancies of four, and the postions refined well with R_1=0.165 and R_2= 0.142. These are the lowest indices achieved in this study.

Because both of the selenium thermal parameters remained high, they were allowed to refine anisotropically. Four cycles of refinement produced no change in either error index.

Various other positions found from the second Fourier map failed, when included in least-squares refinements, to lower R_1 or R_2.

Other trial structures were postulated and refinement attampted, but again no success was achieved in lowering the error indices.

All interpeak distances were calculated, in the hope that enlightening bond lengths might be observed. These distances are recorded in Table 2.

B. Discussion

Most of the models used in the attempted solution of this structure assummed that there might be a Se_8 ring in the large cavity of the zeolite. This was not unreasonably expected since Seff[57] found two S_8 rings in his sulfur complex. Selenium has a greater atomic radius than sulfur, and thus two Se_8 rings could not possibly fit into the large central cavity. Analysis had also indicated approximately eight selenium atoms per unit cell.

The location and the stability of the two H_2O positions indicated that the zeolite was not hydrophobic, as was Seff's complex. The occupancies of the selenium positions correspond well to a total of eight atoms, yet no arrangement of the two positions would significantly lower the error indices or the selenium thermal parameters. The calcium and sodium positions were found and remained stable throughout subsequent refinement.

As became obvious in the structure refinement section, all attempts at locating stable selenium positions which would yield low error indices or thermal parameters successively failed. For this reason, after over 80 cycles of least-

squares analysis, it was decided that the structure was crystallographically disordered. Disorder could in no way be apparent at the onset of this study. After the disorder had been established, however, a review of the Fourier maps lent credence to the belief. Figures 8 thru 12 illustrate the electron density in the center of the zeolite's large cavity. It is believed that selenium and water positions varied in alternating unit cells, giving rise to the disorder.

Table 1. Peak positions from the selenium complex Fourier maps

Peak	Coordinates		
	X	Y	Z
SiAl	0.0	0.1800	0.3700
O(1)	0.0	0.2250	0.5000
O(2)	0.0	0.2900	0.2900
O(3)	0.1000	0.1000	0.3200
Na	0.2200	0.2200	0.2200
Se(1)	0.2500	0.2500	0.5000
Org	0.0	0.0	0.0
X(1)	0.0	0.2600	0.2600
X(2)	o.o	0.4000	0.2600
X(3)	0.0	0.5000	0.4000
X(4)	0.0300	0.5000	0.0300
X(5)	0.1000	0.3000	0.3000
X(6)	0.1300	0.1000	0.1000
X(7)	0.1600	0.4000	0.5000
X(8)	0.2500	0.5000	0.5000
X(9)	0.3000	0.1300	0.3000
X(10)	0.3300	0.3300	0.3300
X(11)	0.3300	0.1300	0.3300
X(12)	0.4000	0.5000	0.1600
X(13)	0.4000	0.5000	0.0
X(14)	0.5000	0.4000	0.1700
X(15)	0.5000	0.2300	0.5000
X(16)	0.5000	0.5000	0.5000

ALL DISTANCES ARE IN Å

	Si,Al	O(1)	O(2)	O(3)	Na	Se(1)	Org.	X(1)	X(2)	X(3)	X(4)	X(5)	X(6)	X(7)	X(8)	X(9)	X(10)	X(11)	X(12)	X(13)	X(14)	X(15)	X(16)
Si,Al	3.29		1.66		3.29			1.66	1.05	3.13	2.46	2.09	3.33			2.33		2.47		3.12			
O(1)	1.68		2.61	2.95				2.97	1.30	2.18	2.42	2.89				3.06		2.42	2.90	2.14			
O(2)	1.66	2.69		2.65	2.95			0.50	1.40	2.40		1.24	3.28			1.60		1.74		2.40			
O(3)	1.68	2.95	2.65		2.41			2.42	2.51		2.51	2.46	2.33					2.87					
Na	3.29		2.95	2.41		3.46		2.78			2.02 →		2.35			1.77	2.33	2.20					
Se(1)		3.08		3.46	3.46	3.12			3.30			3.12		3.48	3.06	2.92	2.50	2.73	2.14 3.48		2.08	3.07	
Org													2.35										
X(1)	1.66	2.97	0.52	2.42	2.78					3.40			2.80			1.74		2.00		3.40			
X(2)	3.01	1.30	1.40	2.51		3.30		1.71		2.44	3.09			2.88		2.07		2.00		2.94	2.96		
X(3)	3.13	2.14	2.98					3.40	2.11	1.73				1.96	3.30	3.17		2.76	2.61	1.73	2.08	3.07	
X(4)	2.46	2.45		2.52					3.09														
X(5)	2.09	2.87	1.24	2.46	2.02	3.12		1.40	1.80	2.99		3.46	3.21	2.83		.37	2.86	.64	2.83	2.94	2.86		
X(6)	3.33		3.28	2.72	2.35		2.35	2.86				3.48	0.52			3.46							
X(7)		2.90				2.14			2.88	2.61		2.83		1.65	1.64	2.76	3.10	2.80		1.96	1.74	1.49	
X(8)						3.06				2.30							3.07	3.29	O	3.30		.25	3.06
X(9)	2.33	3.06	1.60	2.49	1.77	2.92		1.74	2.07	3.16		3.21	3.23	2.76		2.94		~~2.45~~	2.76	3.17	2.78		
X(10)					2.33	2.56						2.86		3.06	3.10	2.50		2.45	3.06		2.98	3.10 ~~2.48~~	
X(11)	2.48	2.92	1.74	2.84	2.20	2.73		2.00	2.00	2.76				2.28 3.06	3.10	0.52	2.45	3.46	2.28	2.76	2.30		
X(12)		2.90				2.14			2.88	2.61		2.83		O	1.65	2.76	3.06					1.49	
X(13)	3.13	2.14	2.90					3.40	2.44	1.73		2.99		1.96	3.30	3.17			1.96	2.70		3.07	
X(14)		2.99				3.44			2.96	2.08		2.87		1.74	1.57	2.78			1.74			1.43	
X(15)						3.07				3.07				1.49			2.98	~~2.30~~ 2.37	1.49	3.09	1.43		3.31
X(16)															3.06		3.19	3.19	~~1.41~~			3.31	

Table 2. Interpeak distances in the selenium complex Fourier map

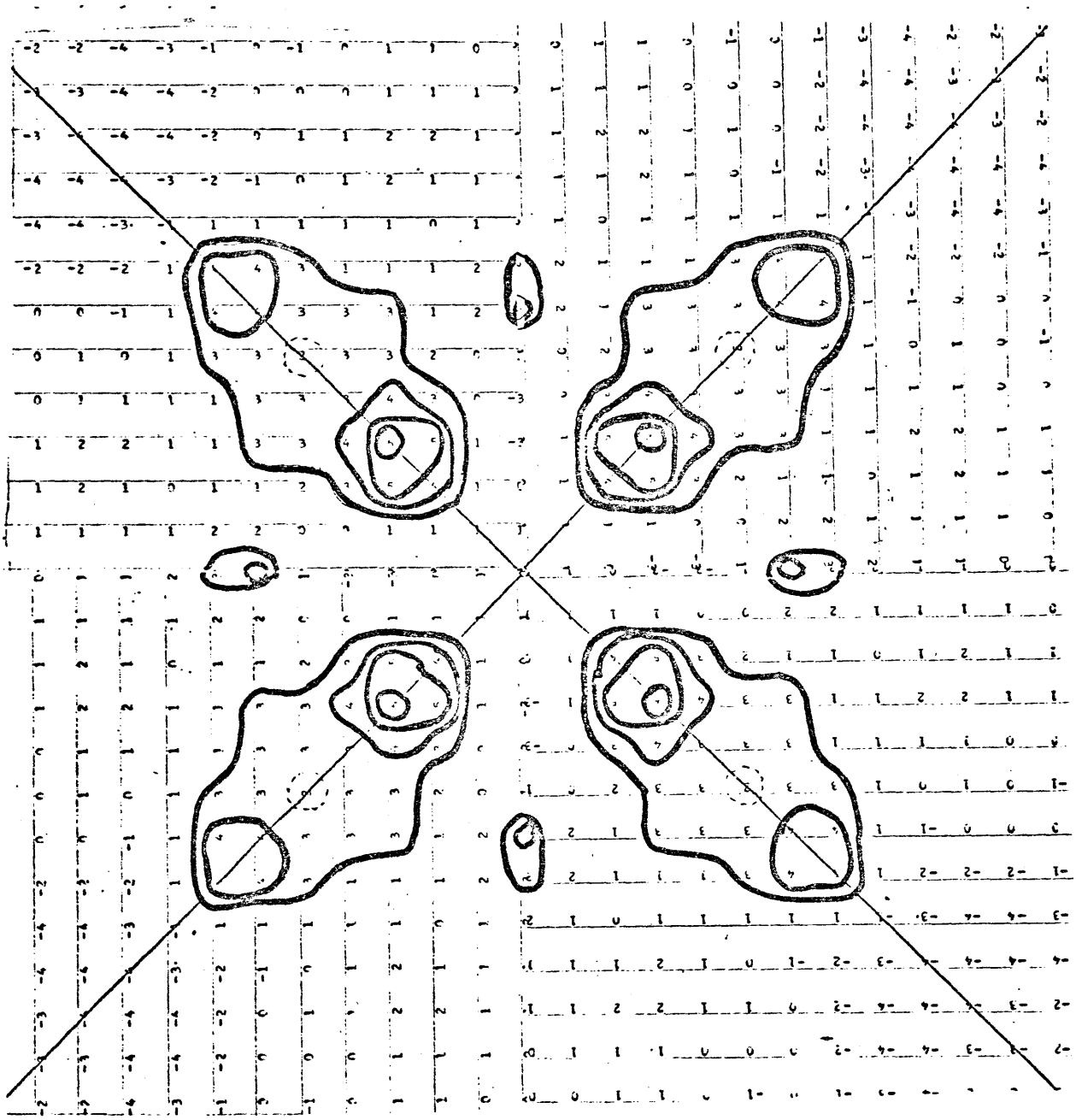


Figure 8. Electron density in the zeolite cavity.

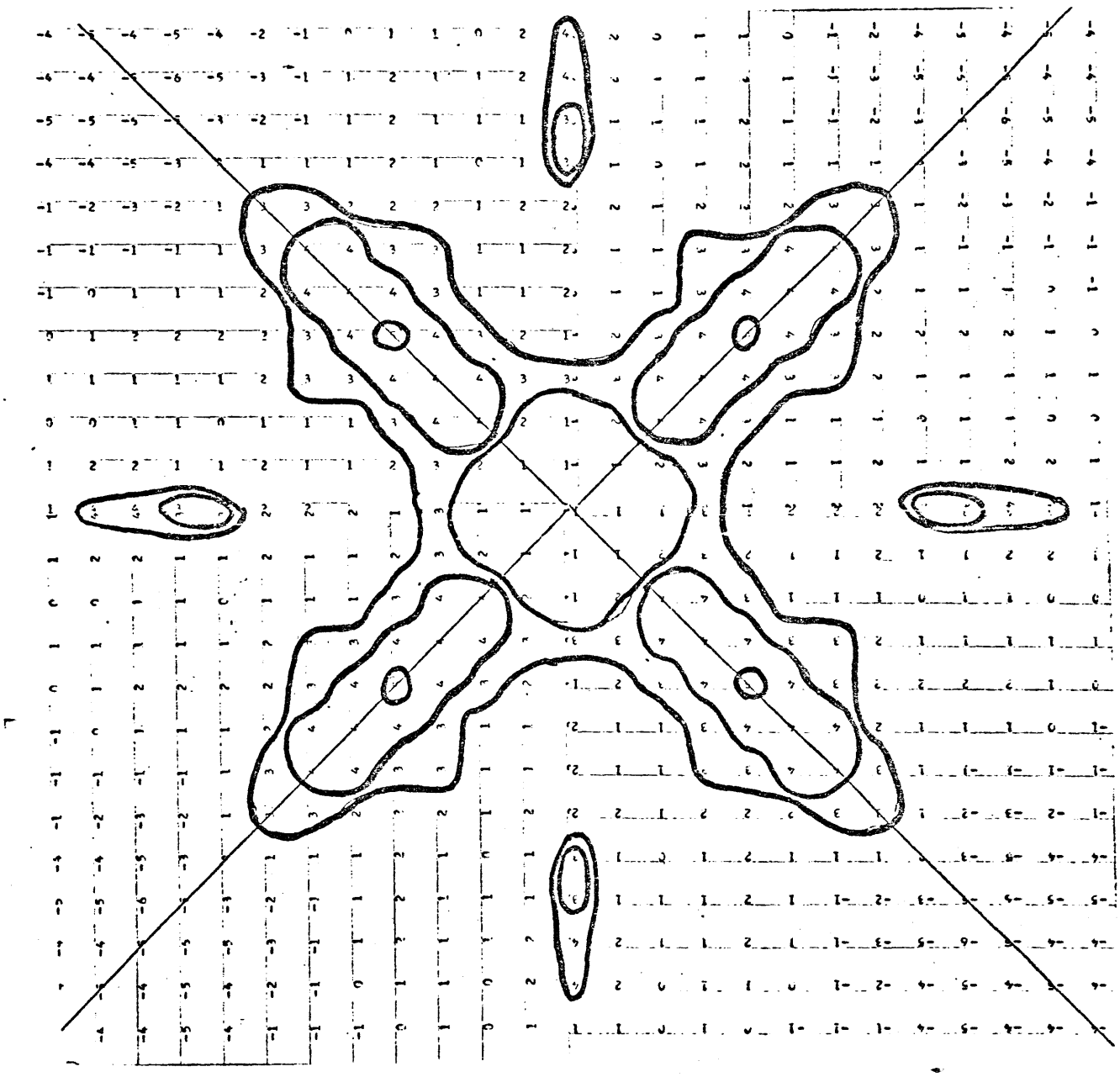


Figure 9. Electron density in the zeolite cavity.

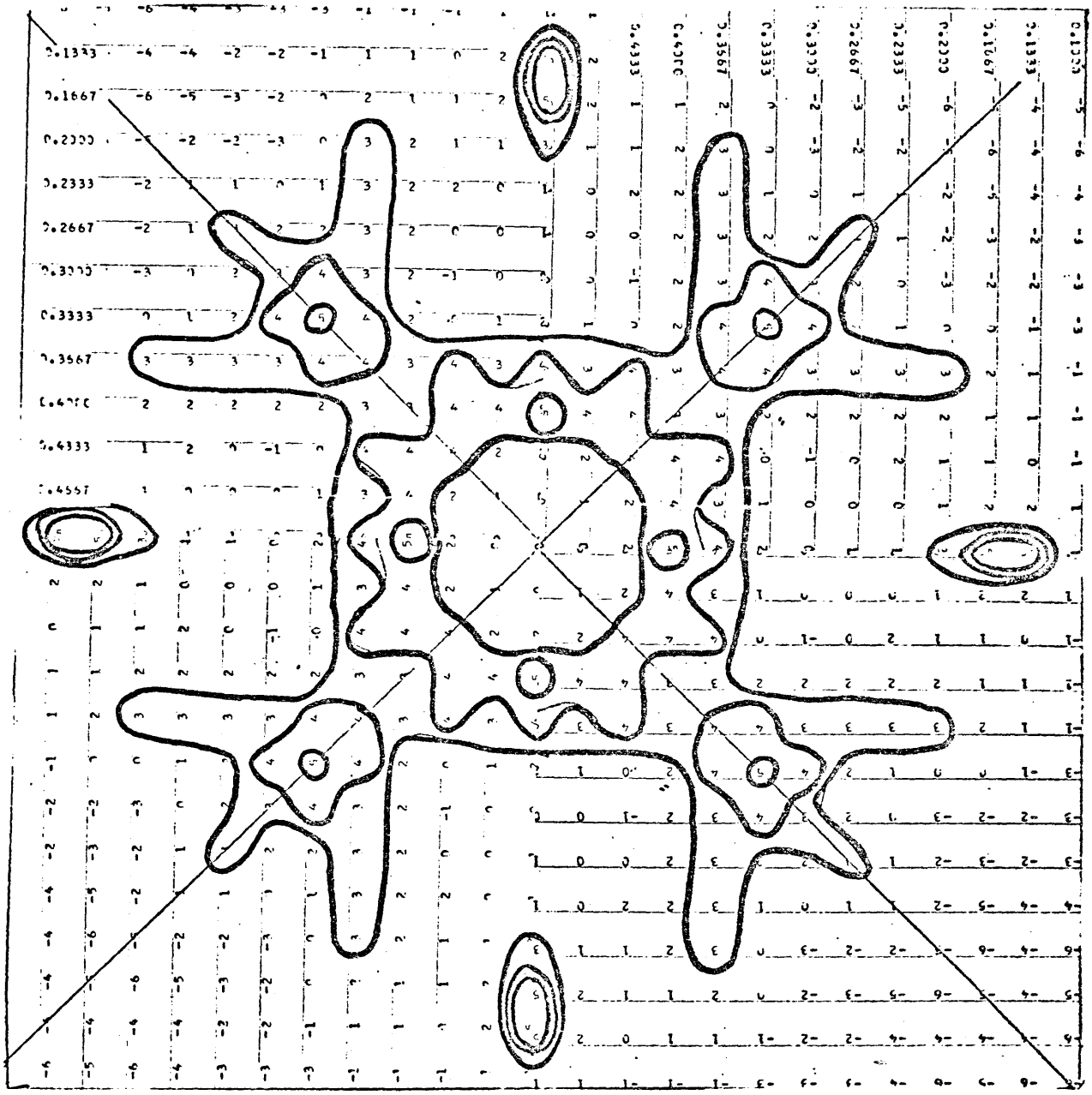


Figure 10. Electron density in the zeolite cavity.

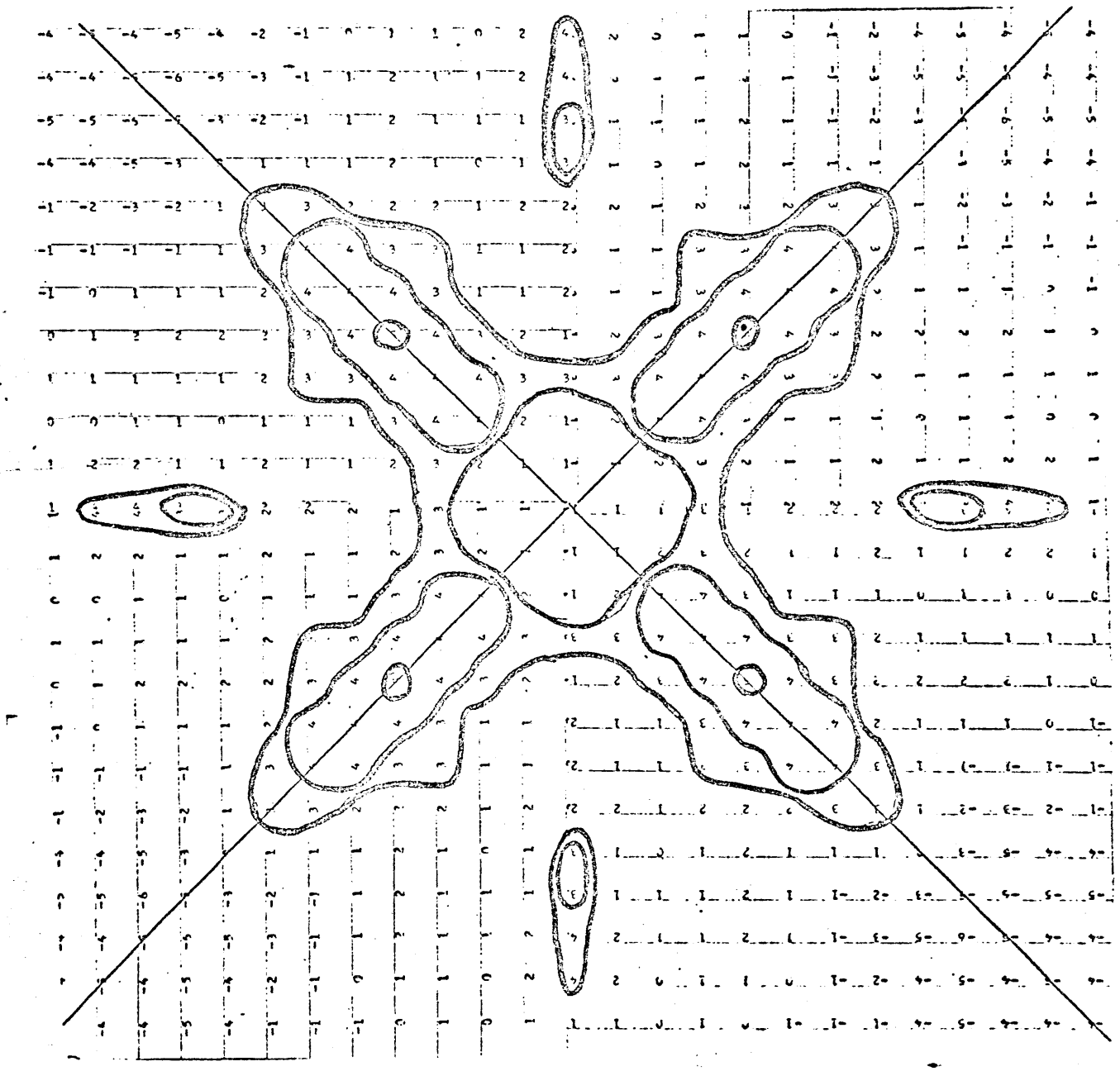


Figure 11. Electron density in the zeolite cavity.

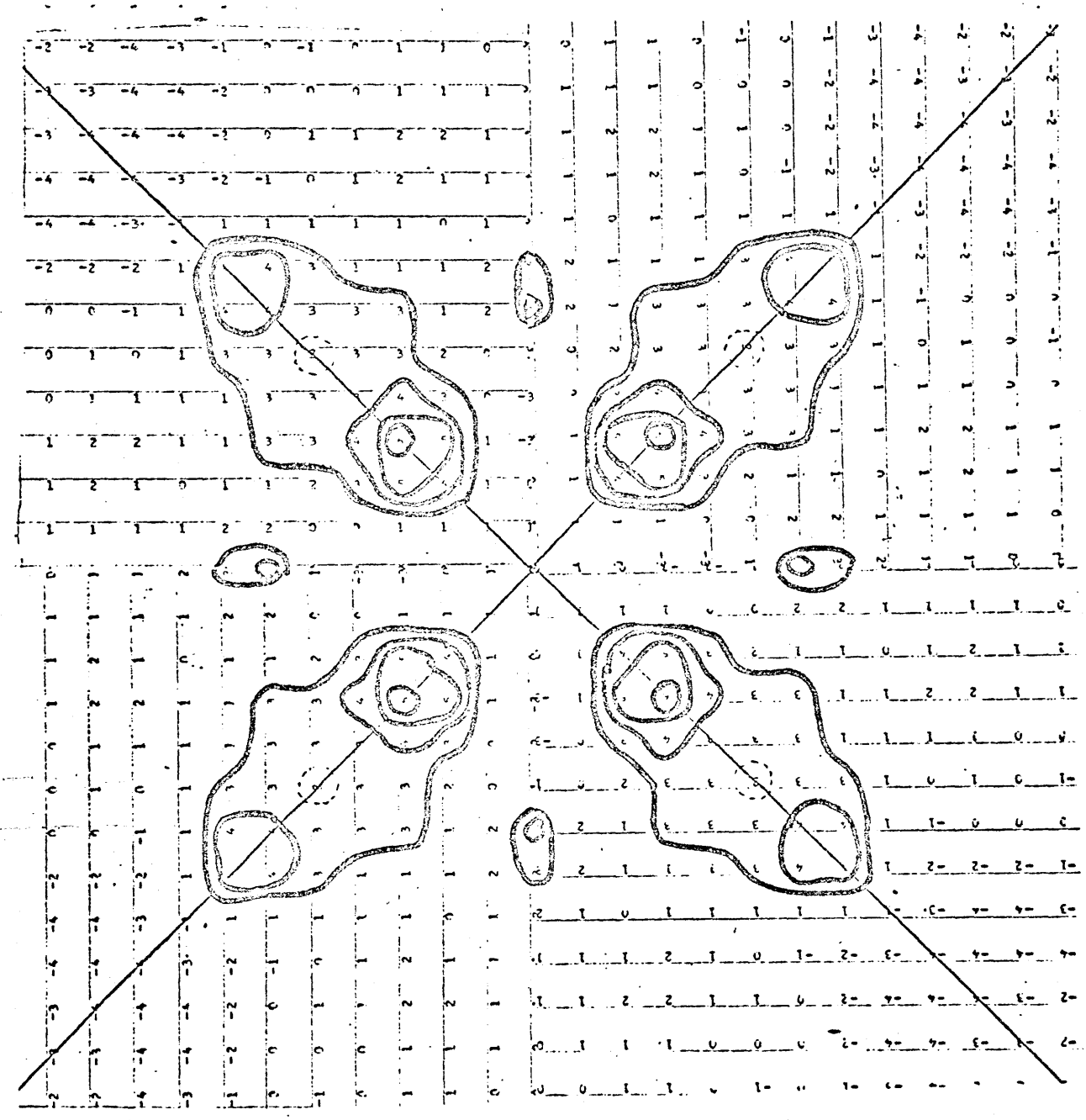


Figure 12. Electron density in the zeolite cavity.

Table 3. Initial refinement of the framework and one sodium position.

SUM FOBS = 5559.813, SUM /DEL F/ = 1173.518, R =0.21107, NO. OF REFL. IN L.S. = 99

THE GENERALIZED WEIGHTED R INDEX (R2) = 0.17489

NORMALIZED SUM OF SQUARES OF RESIDUALS = 125.392.

NEW SCALE FACTOR FOR FOBS = 3.91499. THIS IS (OLD SCALE FACTOR) TIMES G/(G + DELTA G).

ATOM	NEW X	NEW Y	NEW Z	NEW B11 OR B	NEW B22	NEW B33	NEW B12
1	C.152331	C.152331	C.152331	C.085348	0.085348	0.085348	0.177730
2	C.C	0.184591	C.374600	1.4973	0.434485	SIAL	
3	C.C	C.229806	C.500000	1.9552	0.223535	O(1)	NEW B13
4	C.C	C.288621	C.288621	4.2538	0.214940	O(2)	0.177730
5	C.1C81C9	C.1C81C9	0.336910	2.6264	0.446888	O(3)	

Table 4. Refinement with a selenium position and another sodium position, both from the initial Fourier map.

SUM FOBS = 6233.393, SUM /DEL F/ = 1558.550, R = 0.25003, NO. OF REFL. IN L.S. = 99.

THE GENERALIZED WEIGHTED R INDEX (R2) = 0.22529

NORMALIZED SUM OF SQUARES OF RESIDUALS = 261.569.

NEW SCALE FACTOR FOR FOBS = 4.42779. THIS IS (OLD SCALE FACTOR) TIMES G/(G + DELTA G).

ATOM	NEW X	NEW Y	NEW Z	NEW B11 OR B	NEW B22	NEW B33	NEW B12
1	-C.323841	-C.323841	-C.323841	1.421806	1.421806	1.421806	C.C
2	C.C	C.185C94	C.373159	1.0990	0.500000	SIAL	
3	C.C	C.230000	C.500000	2.2323	0.250000	O(1)	NEW B13
4	C.C	C.289856	C.289856	6.7731	C.250000	O(2)	C.C
5	C.1C5090	C.1C5090	C.323655	2.5019	0.500000	O(3)	
6	C.22C000	C.22C000	C.22C000	4.0000	C.333333	NA	
7	C.235052	C.500000	0.500000	19.8510	C.333333	SE 1	

Table 5. Refinement with the anisotropic sodium deleted, and a calcium and selenium position added.

SUM FOBS = 5905.500, SUM /DEL F/ = 1170.615, R =0.19822, NO. OF REFL. IN L.S. = 99

THE GENERALIZED WEIGHTED R INDEX (R2) = 0.17944

NORMALIZED SUM OF SQUARES OF RESIDUALS = 148.929.

NEW SCALE FACTOR FOR FOBS = 4.19044. THIS IS (OLD SCALE FACTOR) TIMES G/(G + DELTA G).

ATOM	NEW X	NEW Y	NEW Z	NEW B11 OR B	NEW B22	NEW B33
1	C.C	C.345545	0.345545	30.4020	0.083333	CA
2	C.C	C.184309	0.374115	1.3035	C.500000	SIAL
3	C.C	0.223853	0.500000	3.9794	0.250000	O(1)
4	C.C	C.293891	0.293891	5.4003	0.250000	O(2)
5	C.1C2790	C.10279C	0.329177	3.0354	0.500000	O(3)
6	C.229450	C.229450	0.229450	0.3595	0.083333	NA
7	C.2C9273	C.500000	0.500000	34.1680	0.083333	SE 1
8	C.258967	C.258967	0.500000	6.2165	0.083333	SE 2

Table 6. Refinement with Se(1) off of the three-fold axis.

SUM FOBS = 6169.438, SUM /DEL.F/ = 1281.776, R =0.20776, NO. OF REFL. IN L.S. = 99

THE GENERALIZED WEIGHTED R INDEX (R2) = 0.1929C

NORMALIZED SUM OF SQUARES OF RESIDUALS = 187.841.

NEW SCALE FACTOR FOR FOBS = 4.36525. THIS IS (OLD SCALE FACTOR) TIMES G/(G + DELTA G).

ATOM	NEW X	NEW Y	NEW Z	NEW B11 OR B	NEW B22	NEW B33
1	C.C	0.335855	0.335855	37.2859	0.083333	NA
2	C.C	0.183492	0.373790	1.0858	C.500000	SIAL
3	C.C	0.224170	0.500000	3.1717	0.250000	O(1)
4	C.C	C.300034	C.300034	6.3476	0.250000	O(2)
5	C.1C3220	C.103220	0.330661	2.7543	0.500000	O(3)
6	C.222733	C.222733	C.222733	4.1859	0.083333	CA
7	C.217150	C.433321	0.500000	26.4033	0.083333	SE 1
8	C.256283	0.256283	0.500000	4.3708	0.083333	SE 2

Table 7. Refinement of only the framework and the stable calcium and selenium positions.

SUM FOBS = 6238.328, SUM /DEL F/ = 1395.265, R =0.22366, NO. OF REFL. IN L.S. = 99

THE GENERALIZED WEIGHTED R INDEX (R2) = 0.20004

NORMALIZED SUM OF SQUARES OF RESIDUALS = 206.541.

NEW SCALE FACTOR FOR FOBS = 4.40684. THIS IS (OLD SCALE FACTOR) TIMES G/(G + DELTA G).

ATOM	NEW X	NEW Y	NEW Z	NEW B11 OR B	NEW B22	NEW B33
1	0.0	0.183588	0.372702	1.0933	0.500000	SIAL
2	0.0	0.227529	0.500000	3.0239	0.250000	O(1)
3	0.0	0.294135	0.294135	4.1432	0.250000	O(2)
4	0.104575	0.104575	0.328876	2.9965	0.500000	O(3)
5	0.222629	0.222629	0.222629	5.0654	0.083333	CA
6	0.260062	0.260062	0.500000	11.2367	0.083333	SE 2

Table 8. Refinement showing the high thermal parameter of an additional selenium position.

SUM FOBS = 6438.133, SUM /DEL F/ = 1366.112, R =0.21219, NO. OF REFL. IN L.S. = 99

THE GENERALIZED WEIGHTED R INDEX (R2) = 0.19730

NORMALIZED SUM OF SQUARES OF RESIDUALS = 213.995.

NEW SCALE FACTOR FOR FOBS = 4.53417. THIS IS (OLD SCALE FACTOR) TIMES G/(G + DELTA G).

ATOM	NEW X	NEW Y	NEW Z	NEW B11 OR B	NEW B22	NEW B33
1	0.0	0.182972	0.372283	0.9849	0.500000	SIAL
2	0.0	0.225929	0.500000	3.0818	0.250000	O(1)
3	0.0	0.293432	0.293432	3.9243	0.250000	O(2)
4	0.104782	0.104782	0.328446	2.7992	0.500000	O(3)
5	0.217363	0.217363	0.217363	4.6257	0.083333	CA
6	0.256353	0.256353	0.500000	8.7956	0.083333	SE 2
7	0.329297	0.329297	0.329297	68.4014	0.083333	SE 3

Table 9. High thermal parameter of added selenium does not decrease.

SUM FOBS = 6630.730, SUM /DEL F/ = 1421.978, R =0.21445, NO. OF REFL. IN L.S. = 99

THE GENERALIZED WEIGHTED R INDEX (R2) = 0.19992

NORMALIZED SUM OF SQUARES OF RESIDUALS = 233.069.

NEW SCALE FACTOR FOR FOBS = 4.59421. THIS IS (OLD SCALE FACTOR) TIMES G/(G + DELTA G).

ATOM	NEW X	NEW Y	NEW Z	NEW B11 OR B	NEW B22	NEW B33
1	0.0	0.182811	0.372231	0.9333	0.500000	SIAL
2	0.0	0.225329	0.500000	3.0669	0.250000	O(1)
3	0.0	0.293499	0.293499	3.3437	0.250000	O(2)
4	0.104784	0.104784	0.328622	2.6782	0.500000	O(3)
5	0.216266	0.216266	0.216266	4.3584	0.083333	CA
6	0.255373	0.255373	0.500000	8.1911	0.083333	SE 2
7	0.332647	0.332647	0.385834	56.7975	0.083333	SE 3

Table 10. Refinement after second Fourier map, new positions are atoms 7 and 8.

SUM FOBS = 6841.277, SUM /DEL F/ = 1631.663, R =0.23850, NO. OF REFL. IN L.S. = 99

THE GENERALIZED WEIGHTED R INDEX (R2) = 0.21313

NORMALIZED SUM OF SQUARES OF RESIDUALS = 281.971.

NEW SCALE FACTOR FOR FOBS = 4.81244. THIS IS (OLD SCALE FACTOR) TIMES G/(G + DELTA G).

ATOM	NEW X	NEW Y	NEW Z	NEW B11 OR B	NEW B22	NEW B33
1	0.0	0.182726	0.374149	0.6652	0.500000	SIAL
2	0.0	0.231158	0.500000	1.7509	0.250000	O(1)
3	0.0	0.288546	0.288546	14.2534	0.250000	O(2)
4	0.098582	0.098582	0.328632	2.8594	0.500000	O(3)
5	0.217716	0.217716	0.217716	2.4494	0.083333	CA
6	0.261909	0.261909	0.500000	8.2012	0.083333	SE 1
7	0.341130	0.341130	0.341130	10.0000	0.083333	SE 2
8	0.240178	0.500000	0.500000	15.0000	0.083333	NA

Table 11. Se(2) thermal parameter increasing.

SUM FOBS = 6295.711, SUM /DEL F/ = 1286.061, R =0.20428, NO. OF REFL. IN L.S. = 99

THE GENERALIZED WEIGHTED R INDEX (R2) = 0.19005

NORMALIZED SUM OF SQUARES OF RESIDUALS = 189.869.

NEW SCALE FACTOR FOR FOBS = 4.38421. THIS IS (OLD SCALE FACTOR) TIMES G/(G + DELTA G).

ATOM	NEW X	NEW Y	NEW Z	NEW B11 OR B	NEW B22	NEW B33
1	0.0	0.183963	0.373102	1.1064	0.500000	SIAL
2	0.0	0.227930	0.500000	3.2002	0.250000	O(1)
3	0.0	0.294477	0.294477	7.3846	0.250000	O(2)
4	0.103556	0.103556	0.330483	2.9956	0.500000	O(3)
5	0.222949	0.222949	0.222949	5.3089	0.083333	CA
6	0.261889	0.261889	0.500000	15.1291	0.083333	SE 1
7	0.336780	0.336780	0.336780	44.0553	0.083333	SE 2
8	0.230471	0.500000	0.500000	7.1767	0.083333	NA

Table 12. Refinement with Se(2) off of the three-fold axis.

SUM FOBS = 6110.906, SUM /DEL F/ = 1218.665, R =0.19942, NO. OF REFL. IN L.S. = 99

THE GENERALIZED WEIGHTED R INDEX (R2) = 0.18355

NORMALIZED SUM OF SQUARES OF RESIDUALS = 166.865.

NEW SCALE FACTOR FOR FOBS = 4.28765. THIS IS (OLD SCALE FACTOR) TIMES G/(G + DELTA G).

ATOM	NEW X	NEW Y	NEW Z	NEW B11 OR B	NEW B22	NEW B33
1	0.0	0.184494	0.373322	1.2092	0.500000	SIAL
2	0.0	0.228169	0.500000	3.5932	0.250000	O(1)
3	0.0	0.293023	0.293023	7.7387	0.250000	O(2)
4	0.104051	0.104051	0.331224	2.9436	0.500000	O(3)
5	0.227025	0.227025	0.227025	5.9184	0.083333	CA
6	0.266152	0.266152	0.500000	25.2038	0.083333	SE 1
7	0.293381	0.400271	0.310161	37.7833	0.083333	SE 2
8	0.238446	0.500000	0.500000	4.1082	0.083333	NA

Table 13. Se(2) back on the three-fold axis.

SUM FOBS = 6137.605, SUM /DEL F/ = 1232.426, R =0.20080, NO. OF REFL. IN L.S. = 99

THE GENERALIZED WEIGHTED R INDEX (R2) = 0.18262

NORMALIZED SUM OF SQUARES OF RESIDUALS = 166.624.

NEW SCALE FACTOR FOR FOBS = 4.31672. THIS IS (OLD SCALE FACTOR) TIMES G/(G + DELTA G).

ATOM	NEW X	NEW Y	NEW Z	NEW B11 OR B	NEW B22	NEW B33
1	0.0	0.184292	0.373111	1.1840	0.500000	SIAL
2	0.0	0.228080	0.500000	3.5145	0.250000	O(1)
3	0.0	0.293662	0.293662	7.0793	0.250000	O(2)
4	0.103909	0.103909	0.330784	2.9110	0.500000	O(3)
5	0.226261	0.226261	0.226261	5.8984	0.083333	CA
6	0.267611	0.267611	0.500000	21.8147	0.083333	SE 1
7	0.276989	0.375118	0.375118	32.4892	0.083333	SE 2
8	0.237093	0.500000	0.500000	4.4146	0.083333	NA

Table 14. Refinement with the calcium ion anisotropic.

SUM FOBS = 6048.441, SUM /DEL F/ = 1214.384, R =0.19129, NO. OF REFL. IN L.S. = 99

THE GENERALIZED WEIGHTED R INDEX (R2) = 0.16447

NORMALIZED SUM OF SQUARES OF RESIDUALS = 144.391.

NEW SCALE FACTOR FOR FOBS = 4.47743. THIS IS (OLD SCALE FACTOR) TIMES G/(G + DELTA G).

ATOM	NEW X	NEW Y	NEW Z	NEW B11 OR B	NEW B22	NEW B33	NEW B12
1	0.225523	0.225523	0.225523	0.021206	0.021206	0.021206	0.045763
2	0.0	0.183877	0.373814	1.2135	0.500000	SIAL	
3	0.0	0.226536	0.500000	2.8617	0.250000	O(1)	
4	0.0	0.293136	0.293136	6.6692	0.250000	O(2)	
5	0.105919	0.105919	0.332218	2.2633	0.500000	O(3)	
6	0.273157	0.273157	0.500000	29.0887	0.083333	SE 1	
7	0.274345	0.390392	0.390392	29.9123	0.083333	SE 2	
8	0.241000	0.500000	0.500000	3.1859	0.083333	NA	

Table 15. Both selenium positions with increasing thermal parameters.

SUM FOBS = 6531.133, SUM /DEL F/ = 1308.185, R =0.20030, NO. OF REFL. IN L.S. = 99

THE GENERALIZED WEIGHTED R INDEX (R2) = 0.17109

NORMALIZED SUM OF SQUARES OF RESIDUALS = 165.594.

NEW SCALE FACTOR FOR FOBS = 4.59005. THIS IS (OLD SCALE FACTOR) TIMES G/(G + DELTA G).

ATOM	NEW X	NEW Y	NEW Z	NEW B11 OR B	NEW B22	NEW B33	NEW B12
1	0.222918	0.222918	0.222918	0.023990	0.023990	0.023990	0.052010
2	0.0	0.184076	0.373672	1.2611	0.500000	SIAL	
3	0.0	0.225561	0.500000	2.7874	0.250000	O(1)	
4	0.0	0.290585	0.290585	6.1134	0.250000	O(2)	
5	0.106578	0.106578	0.332453	2.0813	0.500000	O(3)	
6	0.268944	0.268944	0.500000	37.3419	0.166666	SE 1	
7	0.258211	0.380451	0.380451	41.0761	0.166666	SE 2	
8	0.241643	0.500000	0.500000	2.9573	0.083333	NA	

Table 16. Refinement with 8 H_2O included.

SUM FOBS = 6345.832, SUM /DEL F/ = 1117.085, R =0.17604, NO. OF REFL. IN L.S. = 99

THE GENERALIZED WEIGHTED R INDEX (R2) = 0.15063

NORMALIZED SUM OF SQUARES OF RESIDUALS = 121.185.

NEW SCALE FACTOR FOR FOBS = 4.52492. THIS IS (OLD SCALE FACTOR) TIMES G/(G + DELTA G).

ATOM	NEW X	NEW Y	NEW Z	NEW B11 OR B	NEW B22	NEW B33	NEW B12
1	0.219241	0.219241	0.219241	0.019541	0.019541	0.019541	0.041860
2	0.0	0.183226	0.374321	1.3034	0.500000	SIAL	
3	0.0	0.225127	0.500000	3.0568	0.25000	O(1)	
4	0.0	0.292518	0.292518	6.0217	0.250000	O(2)	
5	0.108122	0.108122	0.335265	3.4591	0.500000	O(3)	
6	0.272734	0.272734	0.500000	38.1103	0.083333	SE 1	
7	0.263589	0.381542	0.381542	27.3434	0.083333	SE 2	
8	0.244186	0.500000	0.500000	2.5502	0.083333	NA	
9	0.073198	0.073198	0.073198	-6.3808	0.083333	H2O1	
10	0.091732	0.326400	0.326400	-6.0284	0.083333	H2O2	

Table 17. The H_2O positions refining well.

SUM FOBS = 6303.984, SUM /DEL F/ = 1038.966, R =0.16481, NO. OF REFL. IN L.S. = 99

THE GENERALIZED WEIGHTED R INDEX (R2) = 0.14183

NORMALIZED SUM OF SQUARES OF RESIDUALS = 106.030.

NEW SCALE FACTOR FOR FOBS = 4.45068. THIS IS (OLD SCALE FACTOR) TIMES G/(G + DELTA G).

ATOM	NEW X	NEW Y	NEW Z	NEW B11 OR B	NEW B22	NEW B33	NEW B12
1	0.222819	0.222819	0.222819	0.016460	0.016460	0.016460	0.032418
2	0.0	0.183812	0.373992	1.3372	0.500000	SIAL	
3	0.0	0.225460	0.500000	3.6926	0.250000	O(1)	
4	0.0	0.290030	0.290030	5.8904	0.250000	O(2)	
5	0.111543	0.111543	0.333507	3.4630	0.500000	O(3)	
6	0.276232	0.276232	0.500000	36.2648	0.083333	SE 1	
7	0.267955	0.385230	0.385230	28.4779	0.083333	SE 2	
8	0.242278	0.500000	0.500000	2.7227	0.083333	NA	
9	0.086757	0.086757	0.086757	0.2740	0.083333	H201	
10	0.102921	0.319058	0.319058	2.8351	0.083333	H202	

Table 18. Refinement with both selenium positions anisotropic does not significantly alter R_1 or R_2.

SUM FOBS = 6308.984, SUM /DEL F/ = 1031.900, R =0.16356, NO. OF REFL. IN L.S. = 99

THE GENERALIZED WEIGHTED R INDEX (R2) = 0.14017

NORMALIZED SUM OF SQUARES OF RESIDUALS = 103.722.

NEW SCALE FACTOR FOR FOBS = 4.42218. THIS IS (OLD SCALE FACTOR) TIMES G/(G + DELTA G).

ATOM	NEW X	NEW Y	NEW Z	NEW B11 OR B	NEW B22	NEW B33	NEW B12
1	0.224789	0.224789	0.224789	0.019921	0.019921	0.019921	0.040366
2	0.274161	0.274161	0.500000	0.053469	0.040432	0.134663	0.0
3	0.272380	0.392102	0.392102	0.074763	0.088655	0.040416	-0.085494
4	0.0	0.183202	0.374165	1.3472	0.500000	SIAL	
5	0.0	0.227328	0.500000	3.6569	0.250000	O(1)	
6	0.0	0.293379	0.293379	7.0302	0.250000	O(2)	
7	0.110885	0.110885	0.332932	3.5093	0.500000	O(3)	
8	0.247891	0.500000	0.500000	2.3009	0.083333	NA	
9	0.091242	0.091242	0.091242	0.5048	0.083333	H201	
10	0.123063	0.327923	0.327923	4.8131	0.083333	H202	

Table 19. Still no anisotropic selenium refinement.

SUM FOBS = 6267.867, SUM /DEL F/ = 1035.801, R =0.16526, NO. OF REFL. IN L.S. = 99

THE GENERALIZED WEIGHTED R INDEX (R2) = 0.14158

NORMALIZED SUM OF SQUARES OF RESIDUALS = 104.448.

NEW SCALE FACTOR FOR FOBS = 4.49588. THIS IS (OLD SCALE FACTOR) TIMES G/(G + DELTA G).

ATOM	NEW X	NEW Y	NEW Z	NEW B11 OR B	NEW B22	NEW B33	NEW B12
1	0.219452	0.219452	0.219452	0.020160	0.020160	0.020160	0.041138
2	0.254287	0.254287	0.500000	-0.077981	0.136610	0.338490	0.0
3	0.264328	0.392403	0.392403	-0.025615	0.046295	0.046807	-0.318897
4	0.0	0.183093	0.374095	1.3133	0.500000	SIAL	
5	0.0	0.226753	0.500000	3.4825	0.250000	O(1)	
6	0.0	0.292549	0.292549	5.8851	0.250000	O(2)	
7	0.108660	0.108660	0.333376	3.1104	0.500000	O(3)	
8	0.250808	0.500000	0.500000	2.0621	0.083333	NA	
9	0.090827	0.090827	0.090827	0.4476	0.083333	H201	
10	0.157703	0.329783	0.329783	0.1667	0.083333	H202	

Table 20. Refinement with a planar Se_8 ring as the species within the large cavity.

SUM FOBS = 6632.188, SUM /DEL F/ = 1326.468, R =0.20000, NO. OF REFL. IN L.S. = 99

THE GENERALIZED WEIGHTED R INDEX (R2) = 0.17572

NORMALIZED SUM OF SQUARES OF RESIDUALS = 180.137.

NEW SCALE FACTOR FOR FOBS = 4.67098. THIS IS (OLD SCALE FACTOR) TIMES G/(G + DELTA G).

ATOM	NEW X	NEW Y	NEW Z	B11 OR B	B22 OR OCC	NEW B33
1	0.0	0.183652	0.372515	0.9798	0.500000	SIAL
2	0.0	0.229734	0.500000	4.6536	0.250000	O(1)
3	0.0	0.289637	0.289637	7.4614	0.250000	O(2)
4	0.109881	0.109881	0.344413	5.3008	0.500000	O(3)
5	0.214146	0.214146	0.214146	5.7950	0.166600	NA
6	0.298625	0.298625	0.500000	23.7782	0.083333	SE1
7	0.110536	0.110536	0.110536	0.2142	0.166666	H201
8	0.0	0.0	0.0	16.6594	0.020830	CA1
9	0.500000	0.299493	0.500000	44.2746	0.083333	SE2

VI. THE STRUCTURE DETERMINATION OF $Zn_5Na_2(A)\cdot H_2O$

A. Structure Refinement

The output of the LPCOR computer program indicated that of 902 reflections, 179 were significant.

Initial least-squares refinement based upon the framework and two anisotropic zinc positions found in Amaro's[43] partially dehydrated zinc exchanged zeolite A, converged in four cycles to an R_1 of 0.24 and an R_2 of 0.20. An additional four cycles of refinement lowered the error indices R_1 and R_2 to 0.21 and 0.18 respectively.

Because its anisotropic thermal parameters were becoming unrealistic, the zinc position at .16, .16, .16, was deleted. The single zinc position remaining, and the framework, refined to an R_1 of 0.21 and an R_2 of 0.18. At this point a three-dimensional electron density Fourier map was produced. A large peak at the origin was assinged as a zinc position and indeed, when this was included in least-squares refinement, R_1 dropped to 0.14 and R_2 to 0.13. In subsequent trial structures two other positions in the sodalite cavity were refined. These positions, which were first thought to be acetylene carbon positions, were assigned occupancies of 4, and considered to be H_2O molecules.

Because it was suspected that there might be no acetylene at all in the zeolite, it was decided to assume that the structure was completely hydrated. Accordingly, all of the peak postions not yet refined from the Fourier map were included in least-squares refinement as H_2O positions.

Table 31 presents the refined postions of these peaks, and with this hydrated trial structure, R_1 and R_2 both decreased to 0.10. A seventh H_2O position was included in four final cycles of full-matrix least-squares, and produced final error indices of 0.097 and 0.092 for R_1 and R_2, respectively.

B. Discussion.

Crystallographic analysis has indicated that no acetylene entered the zeolite. Instead, the zinc exchanged crystal remained completely hydrated. In light of the dehydration procedure employed, it is obvious that this complex is very hydrophilic. Four H_2O molecules are tetrahedraaly bound to the sodalite zinc, and twentyfive additional H_2O molecules are found in the remainder of the unit cell. A portion of the Fourier map generated in this structure determination is reproduced in Figure 13. It clearly indicates the zinc position at the origin (in the center of the sodalite unit) and the water molecules associated with it. Final molecular geometries and distances are given in Table 33 and Table 34, respectively. Tables 21 thru 32 follow the course of the structure solution. A XORTEP computer plotter drawing, showing the framework, zinc, and water positions is presented in Figure 14.

Figure 13. A portion of the Fourier map showing the zinc electron density at the origin, and the associated H_2O positions.

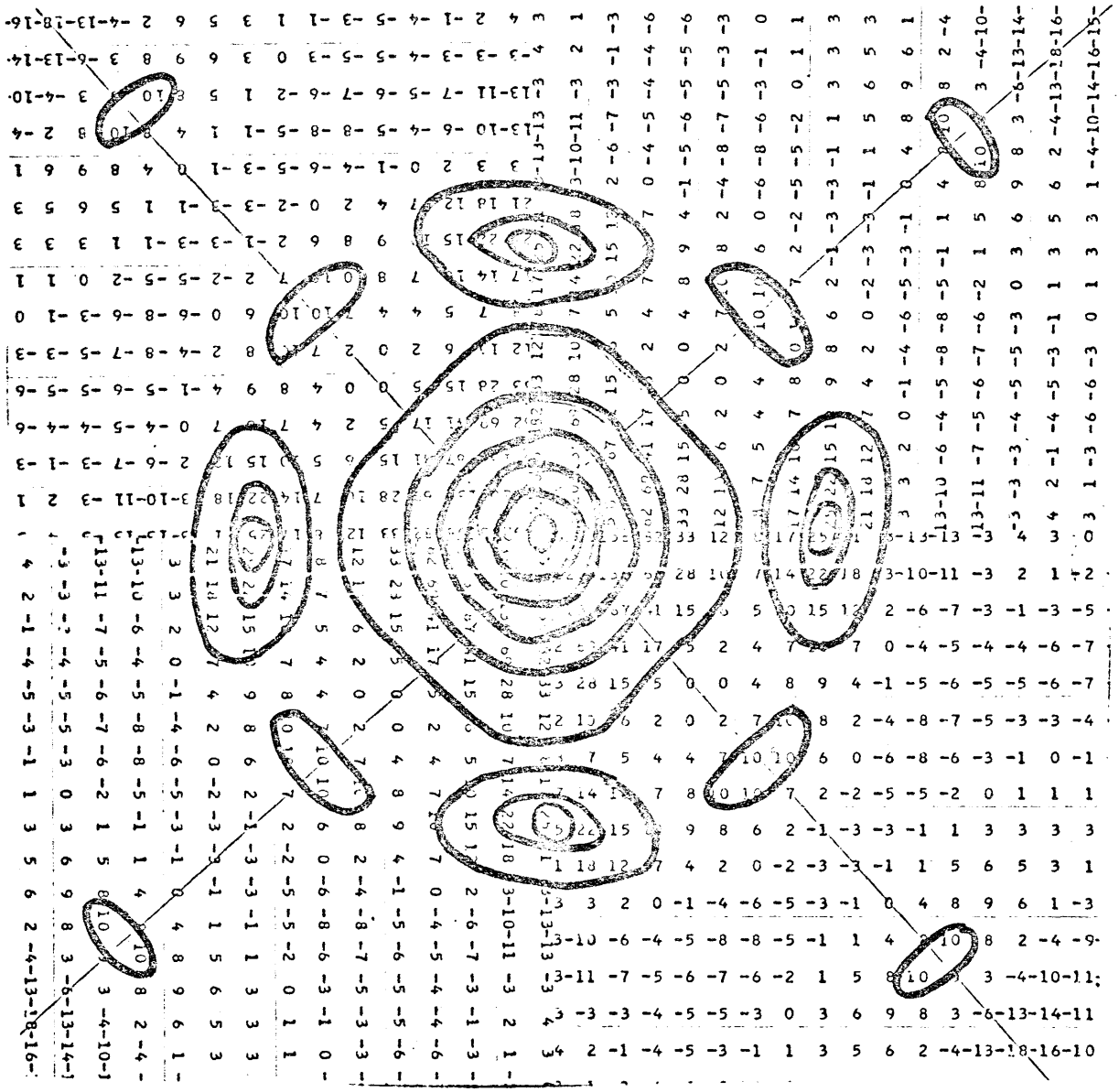


Table 33. Molecular Geometry in the Zinc-Exchanged Zeolite

Selected interatomic angles

Atom A	Atom B	Atom C	Angle in degrees	Deviation
O(1)	SiAl	O(2)	111.19	.69
O(1)	SiAl	O(3)	111.51	.70
O(2)	SiAl	O(3)	106.71	.85
O(3)	SiAl	O(3)	108.92	1.17
SiAl	O(1)	SiAl	157.81	.63
SiAl	O(2)	SiAl	154.56	1.18
SiAl	O(3)	SiAl	139.47	1.19
O(3)	H201	O(3)	86.24	2.15
O(3)	Zn(1)	O(3)	114.48	1.22
O(3)	H203	O(3)	63.42	2.02
O(3)	H202	O(3)	78.83	1.42
H201	Zn(1)	H203	171.87	.89
H206	H205	H207	96.31	2.15
O(2)	H206	H205	97.54	.48
O(1)	H204	O(2)	45.01	1.09
O(1)	H204	H203	102.55	3.36
O(1)	H207	H205	104.58	2.48
O(3)	Zn(1)	H203	103.88	2.34
H204	H203	H207	89.40	2.76
H204	H202	H207	75.42	3.21

Table 34. Selected Interatomic Distances, in Angstroms.

Atom A	Atom B	Distance	Deviation
O(1)	SiAl	1.635	.005
O(2)	SiAl	1.645	.005
O(3)	SiAl	1.676	.006
H201	O(3)	2.763	.049
H201	Zn(1)	2.437	.069
H201	Zn(2)	3.060	.013
H202	O(3)	2.974	.062
H202	H204	3.062	.066
H203	O(3)	3.592	.100
H203	Zn(1)	2.316	.125
H203	H204	2.679	.066
H204	O(3)	3.300	.090
H204	O(2)	3.792	.066
H205	H207	2.393	.116
H206	O(2)	3.542	.019
H207	O(1)	3.303	.127
H207	H202	2.712	.052

Table 21. Initial refinement with only framework and two zinc locations included.

SUM FOBS = 9591.324, SUM /DEL F/ = 2254.190, R =0.23502, NO. OF REFL. IN L.S. = 179

THE GENERALIZED WEIGHTED R INDEX (R2) = 0.19724

NORMALIZED SUM OF SQUARES OF RESIDUALS = 143.060.

NEW SCALE FACTOR FOR FOBS = 3.54284. THIS IS (OLD SCALE FACTOR) TIMES G/(G + DELTA G).

ATOM	NEW X	NEW Y	NEW Z	B11 OR B	B22 OR OCC	NEW B33	NEW B12
1	0.214213	0.214213	0.214213	0.001792	0.001792	0.001792	0.001691
2	0.156547	0.156547	0.156547	0.022435	0.022435	0.022435	0.025321
3	0.0	0.179661	0.367548	0.9198	0.500000	SIAL	
4	0.0	0.202269	0.500000	3.1895	0.250000	O(1)	
5	0.0	0.300716	0.300716	0.8061	0.250000	O(2)	
6	0.115383	0.115383	0.322197	2.6803	0.500000	O(3)	

Table 22. Four more cycles with the just refined positions.

SUM FOBS = 10038.273, SUM /DEL F/ = 2167.830, R =0.21596, NO. OF REFL. IN L.S. = 179

THE GENERALIZED WEIGHTED R INDEX (R2) = 0.17943

NORMALIZED SUM OF SQUARES OF RESIDUALS = 129.684.

NEW SCALE FACTOR FOR FOBS = 3.68480. THIS IS (OLD SCALE FACTOR) TIMES G/(G + DELTA G).

ATOM	NEW X	NEW Y	NEW Z	B11 OR B	B22 OR OCC	NEW B33	NEW B12
1	0.214656	0.214656	0.214656	0.003178	0.003178	0.003178	0.001829
2	0.167606	0.167606	0.167606	0.007010	0.007010	0.007010	-0.001003
3	0.0	0.180887	0.367292	0.8152	0.500000	SIAL	
4	0.0	0.206484	0.500000	2.5704	0.250000	O(1)	
5	0.0	0.300710	0.300710	0.9369	0.250000	O(2)	
6	0.112793	0.112793	0.323006	2.6587	0.500000	O(3)	

Table 23. Refinement with only one zinc location.

SUM FOBS = 10722.238, SUM /DEL F/ = 2457.818, R =0.22923, NO. OF REFL. IN L.S. = 179

THE GENERALIZED WEIGHTED R INDEX (R2) = 0.19363

NORMALIZED SUM OF SQUARES OF RESIDUALS = 172.306.

NEW SCALE FACTOR FOR FOBS = 3.93113. THIS IS (OLD SCALE FACTOR) TIMES G/(G + DELTA G).

ATOM	NEW X	NEW Y	NEW Z	B11 OR B	B22 OR OCC	NEW B33	NEW B12
1	0.213727	0.213727	0.213727	0.005729	0.005729	0.005729	0.004549
2	0.0	0.180177	0.366840	0.6156	0.500000	SIAL	
3	0.0	0.202287	0.500000	2.3647	0.250000	O(1)	
4	0.0	0.300316	0.300316	0.6594	0.250000	O(2)	
5	0.112380	0.112380	0.323129	2.4529	0.500000	O(3)	

Table 24. Four more cycles to refine this position.

SUM FOBS = 9882.695, SUM /DEL F/ = 2077.057, R =0.21017, NO. OF REFL. IN L.S. = 179

THE GENERALIZED WEIGHTED R INDEX (R2) = 0.17930

NORMALIZED SUM OF SQUARES OF RESIDUALS = 125.508.

NEW SCALE FACTOR FOR FOBS = 3.62617. THIS IS (OLD SCALE FACTOR) TIMES G/(G + DELTA G).

ATOM	NEW X	NEW Y	NEW Z	B11 OR B	B22 OR OCC	NEW B33	NEW B12
1	0.213737	0.213737	0.213737	0.003573	0.003573	0.003573	0.003498
2	0.0	0.180584	0.366950	0.8733	0.500000	SIAL	
3	0.0	0.203683	0.500000	2.7427	0.250000	O(1)	
4	0.0	0.300831	0.300831	1.0658	0.250000	O(2)	
5	0.112629	0.112629	0.323088	2.9083	0.500000	O(3)	

Table 25. Refinement with a zinc at the origin (found in the Fourier map).

SUM FOBS = 10455.547, SUM /DEL F/ = 1508.700, R =0.14430, NO. OF REFL. IN L.S. = 179

THE GENERALIZED WEIGHTED R INDEX (R2) = 0.13241

NORMALIZED SUM OF SQUARES OF RESIDUALS = 76.617.

NEW SCALE FACTOR FOR FOBS = 3.83644. THIS IS (OLD SCALE FACTOR) TIMES G/(G + DELTA G).

ATOM	NEW X	NEW Y	NEW Z	B11 OR B	B22 OR OCC	NEW B33	NEW B12
1	0.213133	0.213133	0.213133	0.003261	0.003261	0.003261	0.004004
2	0.0	0.181277	0.366727	0.8104	0.500000	SIAL	
3	0.0	0.201652	0.500000	2.2723	0.250000	O(1)	
4	0.0	0.301884	0.301884	1.8891	0.250000	O(2)	
5	0.112445	0.112445	0.323701	3.2326	0.500000	O(3)	
6	0.0	0.0	0.0	3.5218	0.020833	ZN(2	

Table 26. An additional four H_2O molecules have been included in the sodalite unit, on the three-fold axis.

SUM FOBS = 10386.180, SUM /DEL F/ = 1354.372, R =0.13040, NO. OF REFL. IN L.S. = 179

THE GENERALIZED WEIGHTED R INDEX (R2) = 0.12380

NORMALIZED SUM OF SQUARES OF RESIDUALS = 66.089.

NEW SCALE FACTOR FOR FOBS = 3.81113. THIS IS (OLD SCALE FACTOR) TIMES G/(G + DELTA G).

ATOM	NEW X	NEW Y	NEW Z	B11 OR B	B22 OR OCC	NEW B33	NEW B12
1	0.213124	0.213124	0.213124	0.003326	0.003326	0.003326	0.004061
2	0.0	0.181386	0.366631	0.8383	0.500000	SIAL	
3	0.0	0.201698	0.500000	2.3549	0.250000	O(1)	
4	0.0	0.301732	0.301732	1.8632	0.250000	O(2)	
5	0.114197	0.114197	0.323563	3.3471	0.500000	O(3)	
6	0.0	0.0	0.0	3.4595	0.020833	ZN(2	
7	0.081541	0.081541	0.081541	5.9501	0.083333	H2O1	

Table 27. Refinement with the sodalite waters taken off of the three-fold axis.

SUM FOBS = 10414.047, SUM /DEL F/ = 1346.603, R =0.12931, NO. OF REFL. IN L.S. = 179

THE GENERALIZED WEIGHTED R INDEX (R2) = 0.12338

NORMALIZED SUM OF SQUARES OF RESIDUALS = 65.993.

NEW SCALE FACTOR FOR FOBS = 3.81919. THIS IS (OLD SCALE FACTOR) TIMES G/(G + DELTA G).

ATOM	NEW X	NEW Y	NEW Z	B11 OR B	B22 OR OCC	NEW B33	NEW B12
1	0.213100	0.213100	0.213100	0.003344	0.003344	0.003344	0.004164
2	0.0	0.181405	0.366616	0.8356	0.500000	SIAL	
3	0.0	0.201385	0.500000	2.3179	0.250000	O(1)	
4	0.0	0.301570	0.301570	1.7617	0.250000	O(2)	
5	0.114451	0.114451	0.323874	3.3123	0.500000	O(3)	
6	0.0	0.0	0.0	3.5264	0.020833	ZN(2	
7	0.054209	0.095676	0.095676	0.9320	0.083333	H201	

Table 28. Refinement with the sodalite waters back on the three-fold, and four additional waters at .31, .31. .31.

SUM FOBS = 5168.180, SUM /DEL F/ = 625.221, R =0.12098, NO. OF REFL. IN L.S. = 179

THE GENERALIZED WEIGHTED R INDEX (R2) = 0.11625

NORMALIZED SUM OF SQUARES OF RESIDUALS = 14.428.

NEW SCALE FACTOR FOR FOBS = 1.89679. THIS IS (OLD SCALE FACTOR) TIMES G/(G + DELTA G).

ATOM	NEW X	NEW Y	NEW Z	B11 OR B	B22 OR OCC	NEW B33	NEW B12
1	0.213381	0.213381	0.213381	0.003385	0.003385	0.003385	0.003763
2	0.0	0.181563	0.366759	0.8345	0.500000	SIAL	
3	0.0	0.201426	0.500000	2.4735	0.250000	O(1)	
4	0.0	0.301382	0.301382	1.9748	0.250000	O(2)	
5	0.113823	0.113823	0.325250	3.8127	0.500000	O(3)	
6	0.0	0.0	0.0	3.3782	0.020833	ZN(2	
7	0.083175	0.083175	0.083175	6.6943	0.083333	H201	
8	0.306486	0.306486	0.306486	4.2901	0.083333	H202	

Table 29. The first H_2O position was at first erroniously called a carbon.

SUM FOBS = 10311.785, SUM /DEL F/ = 1267.169, R =0.12289, NO. OF REFL. IN L.S. = 179

THE GENERALIZED WEIGHTED R INDEX (R2) = 0.11593

NORMALIZED SUM OF SQUARES OF RESIDUALS = 57.124.

NEW SCALE FACTOR FOR FOBS = 3.78348. THIS IS (OLD SCALE FACTOR) TIMES G/(G + DELTA G).

ATOM	NEW X	NEW Y	NEW Z	B11 OR B	B22 OR OCC	NEW B33	NEW B12
1	0.213407	0.213407	0.213407	0.003363	0.003363	0.003363	0.003588
2	0.0	0.181383	0.366799	0.8509	0.500000	SIAL	
3	0.0	0.201745	0.500000	2.5318	0.250000	O(1)	
4	0.0	0.301003	0.301003	1.8039	0.250000	O(2)	
5	0.112810	0.112810	0.325043	3.9592	0.500000	O(3)	
6	0.0	0.0	0.0	3.4373	0.020833	ZN(2	
7	0.083253	0.083253	0.083253	7.0591	0.083333	H2O1	
8	0.312617	0.312617	0.312617	1.0540	0.083333	C(1)	

Table 30. And another carbon was mistakenly assigned a H_2O position.

SUM FOBS = 10329.895, SUM /DEL F/ = 1261.033, R =0.12208, NO. OF REFL. IN L.S. = 179

THE GENERALIZED WEIGHTED R INDEX (R2) = 0.11700

NORMALIZED SUM OF SQUARES OF RESIDUALS = 58.393.

NEW SCALE FACTOR FOR FOBS = 3.78920. THIS IS (OLD SCALE FACTOR) TIMES G/(G + DELTA G).

ATOM	NEW X	NEW Y	NEW Z	B11 OR B	B22 OR OCC	NEW B33	NEW B12
1	0.213398	0.213398	0.213398	0.003323	0.003323	0.003323	0.003548
2	0.0	0.181350	0.366818	0.8456	0.500000	SIAL	
3	0.0	0.201759	0.500000	2.5552	0.250000	O(1)	
4	0.0	0.301057	0.301057	1.7723	0.250000	O(2)	
5	0.112662	0.112662	0.324561	3.9787	0.500000	O(3)	
6	0.0	0.0	0.0	3.4857	0.020833	ZN(2	
7	0.083143	0.083143	0.083143	7.2940	0.083333	H2O1	
8	0.311902	0.311902	0.311902	0.8744	0.083333	C(1)	
9	0.360655	0.360655	0.360655	15.3461	0.083333	C(2)	

Table 31. Reflection 2-10-15 has been deleted. All peaks are added as waters.

SUM FOBS = 11815.066, SUM /DEL F/ = 1231.056, R =0.10419,

HE GENERALIZED WEIGHTED R INDEX (R2) = 0.10164

NORMALIZED SUM OF SQUARES OF RESIDUALS = 31.424.

NEW SCALE FACTOR FOR FOBS = 3.40360. THIS IS (OLD SCALE FACTOR) TIMES G/(G + DELTA G). G IS NOT CHANGED

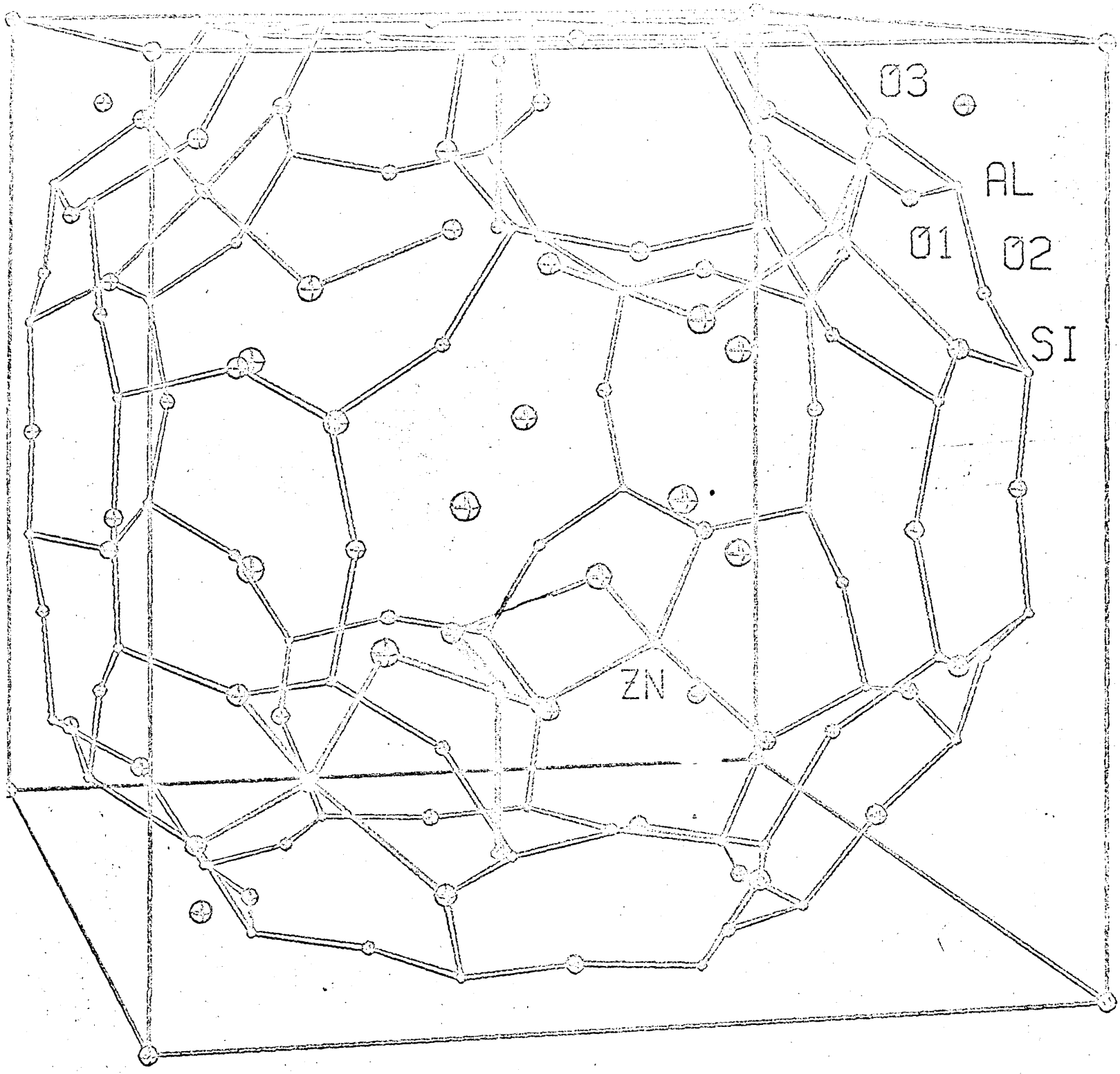
TOM	NEW X	NEW Y	NEW Z	B11 OR B	B22 OR OCC	NEW B33	NEW B12	NEW B13
1	0.210385	0.210385	0.210385	0.004972	0.004972	0.004972	0.004438	0.004438
2	0.0	0.182378	0.368467	0.7907	0.500000	SIAL		
3	0.0	0.208240	0.500000	2.8246	0.250000	O1		
4	0.0	0.296017	0.296017	1.6075	0.250000	O2		
5	0.111402	0.111402	0.330603	3.9551	0.500000	O3		
6	0.0	0.0	0.0	2.9954	0.020833	ZN3		
7	0.312282	0.312282	0.312282	6.1017	0.083333	H203		
8	0.277271	0.277271	0.277271	4.6417	0.083333	H202		
9	0.038975	0.500000	0.500000	1.6862	0.041667	H205		
0	0.217614	0.357260	0.500000	13.7336	0.250000	H204		
1	0.072974	0.108502	0.108502	3.8338	0.125000	H201		
2	0.234595	0.500000	0.500000	1.4853	0.041667	H205		

Table 32. Refinement with the final H_2O position included.

SUM FOBS = 10346.184, SUM /DEL F/ = 1008.768, R =0.09750, NO. OF REFL. IN L.S. = 177

THE GENERALIZED WEIGHTED R INDEX (R2) = 0.09232

ATOM	NEW X	NEW Y	NEW Z	B11 OR B	B22 OR OCC	NEW B33	NEW B12
1	0.213166	0.213166	0.213166	0.003292	0.003292	0.003292	0.003479
2	0.0	0.181707	0.366763	0.8338	0.500000	SIAL	
3	0.0	0.197383	0.500000	2.5752	0.250000	O(1)	
4	0.0	0.301462	0.301462	2.0808	0.250000	O(2)	
5	0.114203	0.114203	0.326737	3.9385	0.500000	O(3)	
6	0.0	0.0	0.0	3.1970	0.020833	ZN2	
7	0.320913	0.320913	0.320913	4.3716	0.083333	H2/3	
8	0.283501	0.283501	0.283501	8.0293	0.083333	H202	
9	0.032696	0.500000	0.500000	2.0292	0.041667	H206	
10	0.204968	0.382736	0.500000	9.8423	0.166667	H204	
11	0.050006	0.098629	0.098629	2.3269	0.125000	H201	
12	0.213333	0.500000	0.500000	3.1600	0.041667	H205	
13	0.306516	0.265477	0.500000	9.9855	0.083333	H207	



HYDRATED $ZN_{5.0}NA_2$-ZEOLITE A

Figure 14. Computer plotter drawing of the hydrated zinc zeolite

VII. SUGGESTIONS FOR FURTHER WORK

The successful preparation of the stoichiometric, divalently exchanged zeolite A in this work will allow future work to proceed in introducing substrate or ligand species into the exchanged zeolite, for the purpose of mimicing the geometry or action of these ionic and ligand entities in biological systems. For instance, the zinc exchanged zeolite could be partially dehydrated and then CO_2 could be introduced into it. Crystallographic study of this complex may then elucidate the mechanism of catalysis of Carbonic Anhydrase, which, containing zinc at its active site, promotes and regulates the equilibrium;

$$CO_2 + H_2O \rightleftharpoons H_2CO_3 .$$

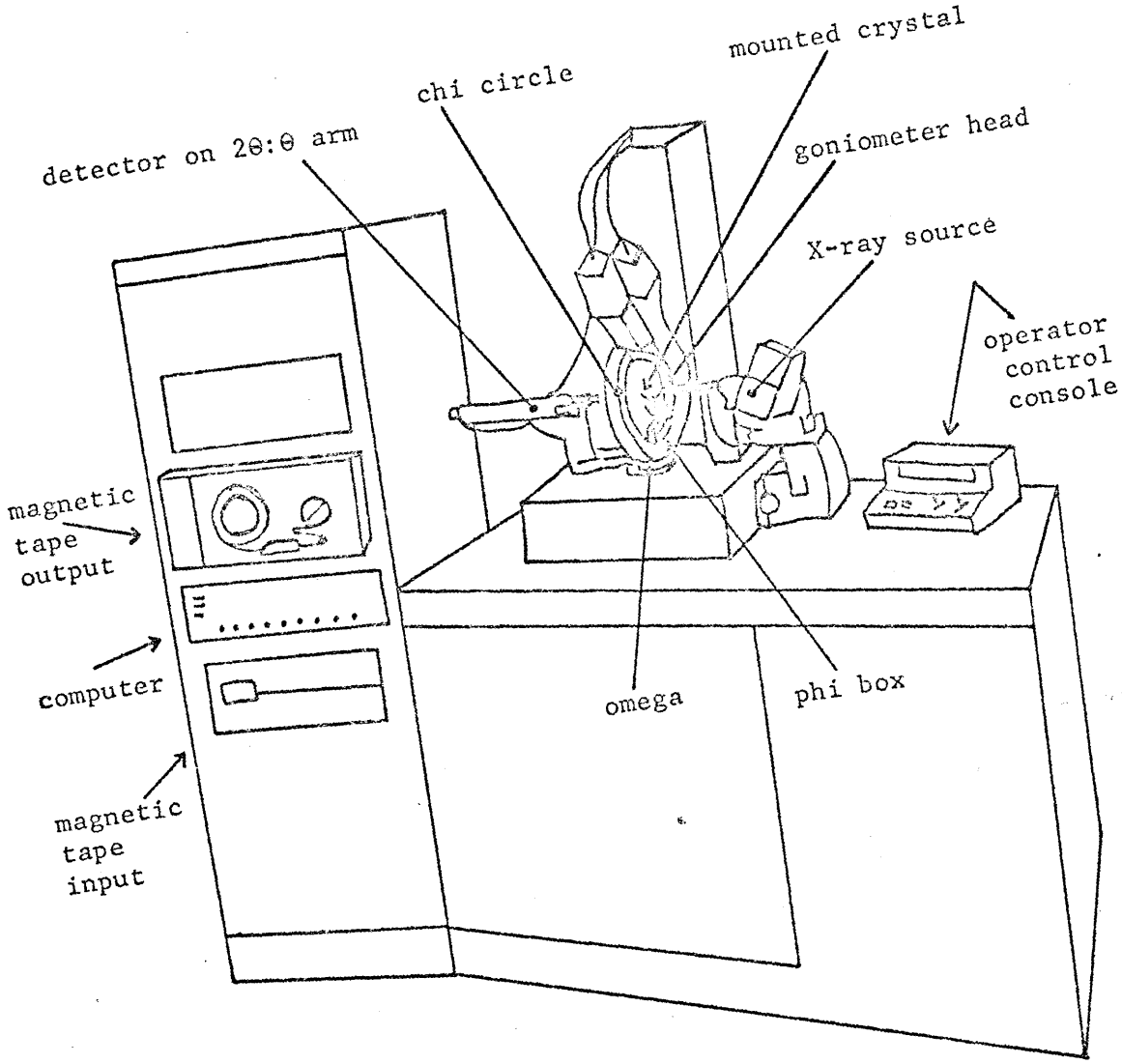
In a similiar manner, the other exchanged zeolites could mimic, upon introduction of specific species, many of the other enzymatic metalloproteins, providing they catalize reactions involving molecules which are small enough to fit into the zeolite cavities. The use of the zeolite complexes in this way, could then quickly and inexpensively produce biological models of enzyme systems which presently are studied crystallographically at the cost of much time and money in entire three-dimensional protein structures. Often, these completed protein structures are still unable to allow postulation of the specific action in catalysis, thus any results at all from a zeolite complex model system would serve to progress the understanding of this catalysis.

The results of the sorption work in this research also encourage further work with these model systems. Although not yet entirely satisfactory, our sorption methods can now be analized and improved.

APPENDIX A

1) The Pl Diffractometer

2) Diffractometer output sample



1) The P1 Diffractometer

```
6676666676666666
    412      828      331       42       19     55.00
    362    2   3       18    64.77    32.38   352.00   348.13     2.44     .50
6666666666666666
    331      672      326        7       18     55.16
    363    2   3       19    68.69    34.35   352.24   347.60     2.47     .50
6666656666666656-
    355      696      365      -12       18     55.33
    364    2   4        4    20.17    10.08   331.73    19.25     2.12     .50
88877878887777777
   1024     2044      912       54       31     55.47
   -365    0   0        6    20.16    10.08   356.96   337.83     2.12     .50
788889ABCDDCA988
   1027    22907     1548    10166       79     55.61
   -365    0   5        5    23.81    11.91   319.44     3.92     2.15     .50
778899ACDDCA9888
    857    17879     1175     7923       70     55.75
    367    2   4        5    22.57    11.29   335.21    13.81     2.14     .50
7777777887777777
    868     1843      757      113       29     55.90
    368    2   4        6    25.22    12.61   337.87     9.42     2.16     .50
7777777777777777
    781     1473      740      -24       27     56.04
    369    2   4        7    28.05    14.03   339.97     5.85     2.17     .50
77778889A9987777
    769     3214      763      845       34     56.19
    370    2   4        8    31.02    15.51   341.67     2.94     2.19     .50
7777777888877777
    674     1826      683      234       28     56.33
    371    2   4        9    34.10    17.05   343.06      .53     2.21     .50
7777777877777777
    748     1482      591       71       26     56.48
    372    2   4       10    37.28    18.64   344.22   353.51     2.23     .50
7777767767766767
    570     1957      504       -8       23     56.63
    373    2   4       11    40.54    20.27   345.21   356.80     2.25     .50
7667666676667666
    456      958      472       15       21     56.78
    374    2   4       12    43.88    21.94   346.06   355.34     2.28     .50
```

2) Diffractometer output sample.

1st row; the reflection peak

2nd row; sequence number, h, k, ℓ, 2θ, ω, ϕ, X, scan range, scan rate

3rd row; left background, scan count, right background, intensity, standard deviation, exposure hours

A negative sign in front of the sequence number designates a check reflection.

APPENDIX B

1) a sample of the LPCOR output

2) a sample of the PACKEM output

3) a sample of the FMLS output

4) a sample of the MGEOM output

Samples of ORTEP and SFC-ALFF Fourier map outputs have already been presented.

```
LINE 1:SEQ.#,H,K,L,I,SIGMAI,2THETA,OMEGA,PHI,CHI,EXP.HOURS,SCANRANGE,SCANRATE,LEFTBKGND,COUNT,RIGHTBKGND
                LINE 2: SCAN PROFILE IN TRUNCATED BASE 2 LOGARITHMS JUST LIKE THE TELETYPE OUTPUT.
                LINE 3:NETCOUNT,CORSIGMAI,LP,DECAY,ABSORP,F,SIGMAF,UBS?

   -1   0   0   6      10422.0    79.7    20.16    10.08  356.96  337.83     0.14      2.123  0.5       1050.      23126.   1232.
3444544444444554555556656666777778888999999000000999999988877766666665655555555555554444444444444
   -2   0   5   5       7943.5    70.6    23.81    11.91  319.44    3.92     0.29      2.146  0.5        960.      17902.   1055.
444342444444444455555556666667777788889999999999999988888777766666565565555555555555544445444444443
    3   0   0   1      19642.0   120.5     3.34     1.67  356.96  337.83     0.42      2.020  0.5       2719.      48688.   6685.
6565666666666666767777777778888889990000000101101000000999988888878777777777777777777777776767
                0   0   1    19644.       513. 17.1156  0.9999  1.0000      33.88      7.58
    4   0   0   2       750.0    70.3     6.69     3.35  356.96  337.83     0.56      2.040  0.5       5110.      10636.   4026.
666666666666666666666666666666766677777777777777777766666666666666666666666666666666666666666
                0   0   2      750.        85.  8.5244  0.9998  1.0000       9.38      4.55
    5   0   0   3       2528.0    70.6    10.04     5.02  356.96  337.83     0.69      2.061  0.5       4099.      12488.   3333.
666656666666666666666666676667777778888888888777777666666666666656665666556666656656
                0   0   3     2529.       121.  5.6460  0.9997  1.0000      21.16      2.86
    6   0   0   4       1189.5    51.9    13.40     6.70  356.96  337.83     0.83      2.081  0.5       2539.      6579.   1661.
555555555555555555565555555556666666667777777777776766666655555555555555555555455555554445544
                0   0   4     1190.        76.  4.1361  0.9995  1.0000      16.84      2.25
    7   0   0   5       3012.0    52.3    16.78     8.39  356.96  337.83     0.97      2.102  0.5       1346.      8492.   1122.
444544444444454544455455555555666677778882888888887777766666555555555554444445444444445344444444
                0   0   5     3014.       113.  3.3179  0.9994  1.0000      30.14      1.87
    8   0   0   6      10459.5    79.6    20.16    10.08  356.96  337.83     1.12      2.123  0.5       1059.      23118.   1140.
444444344444454545555556666677773888899999000000099999988887777766666656555555455544455454444454
                0   0   6    10467.       289.  2.7258  0.9993  1.0000      61.97      2.33
    9   0   0   7        311.5    30.8    23.57    11.78  356.96  337.83     1.26      2.144  0.5        841.      2211.    747.
344433434343334434444434433343344544555555555555455444444444434334333343233334434324433
                0   0   7      312.        37.  2.2977  0.9992  1.0000      11.65      1.59
   10   0   0   8        748.0    33.5    26.99    13.50  356.96  337.83     1.40      2.166  0.5        746.      2991.    749.
434444333443343333444444444444544555666666666665555555545444344334434443434333443334433444
                0   0   8      749.        48.  1.9723  0.9991  1.0000      18.48      1.24
   11   0   0   9        948.5    34.9    30.45    15.22  356.96  337.83     1.55      2.189  0.5        719.      3386.    770.
344434333343444444434443443555555666666666666666655555444444444334343234434433434343333433
                0   0   9      949.        54.  1.7158  0.9990  1.0000      23.52      1.15
   12   0   0  10       2564.0    45.9    33.93    16.96  356.96  337.83     1.70      2.211  0.5        844.      6781.    809.
334444434444443444544545555545555666777777777877777776766666555554444454443443434344334333334
                0   0  10     2567.        97.  1.5079  0.9988  1.0000      41.26      1.18
   13   0   0  11        895.5    32.1    37.44    18.72  356.96  337.83     1.85      2.234  0.5        627.      2954.    536.
333344333233334334443434344443355455555566666666666665565554544344434333433333333433333333433323
                0   0  11      897.        50.  1.3359  0.9987  1.0000      25.91      0.97
   14   0   0  12        -16.5    22.1    40.99    20.49  356.96  337.83     2.00      2.259  0.5        510.      957.     480.
333232323332332323333233322321333033323331223333213233233233333333323333223223323123333432232233
                0   0  12        0.        22.  1.1911  0.9986  1.0000       3.60      3.07U
   15   0   0  13        32.5    21.9    44.58    22.29  356.96  337.83     2.15      2.284  0.5        498.      996.     433.
334233322323333222332223323433332333323334334342324343333333213113333223323322232323223322232
                0   0  13       33.        23.  1.0678  0.9985  1.0000       5.52      2.05U
   16   0   0  14       179.0    23.3    48.21    24.11  356.96  337.83     2.30      2.310  0.5        493.      1262.    411.
224333223333222322233333332123333344454444444444444433343333333232332333323333123333223342122
                0   0  14      179.        27.  0.9619  0.9984  1.0000      13.65      0.99
   17   0   0  15         46.0    20.7    51.90    25.95  356.96  337.83     2.46      2.337  0.5        411.      900.     397.
222223433323333322313322332322322333333332232222333223232333333333332233311233332323233333232322
                0   0  15       46.        22.  0.8705  0.9983  1.0000       7.28      1.49U
   18   0   0  16       240.0    23.2    55.65    27.83  356.96  337.83     2.62      2.365  0.5        436.      1313.    397.
222232233222232332212333332333344433444545444444444453344443324433333233123223233333332232223333
                0   0  16      240.        28.  0.7913  0.9981  1.0000      17.43      0.80
   19   0   0  17        -4.0    20.3    59.47    29.73  356.96  337.83     2.78      2.395  0.5        411.      822.     419.
223233333222322322332223333233333333312223332323323222313221232232222212222123323123 2
                0   0  17        0.        20.  0.7230  0.9980  1.0000       4.44      2.29U
   20   0   0  18        -8.5    19.5    63.36    31.68  356.96  337.83     2.94      2.427  0.5        407.      751.     361.
232232232222223112232113233332322233332122122322333123333232122323222322322322212321333223223222 1
```

1). LPCOR computer program output.

F66-LEVEL LINKAGE EDITOR OPTIONS SPECIFIED NONE
DEFAULT OPTION(S) USED - SIZE=(94208,49152)
****USERPROG DOES NOT EXIST BUT HAS BEEN ADDED TO DATA SET

0	0	1	33.88	7.5800	0	0	2	9.38	4.5500	0	0	3	21.16	2.8600
0	0	4	16.84	2.2500	0	0	5	30.14	1.8700	0	0	6	61.97	2.3300
0	0	7	11.65	1.5900	0	0	8	19.48	1.2400	0	0	9	23.52	1.1500
0	0	10	41.26	1.1800	0	0	11	25.91	0.9700	0	0	14	13.65	0.9800
0	0	16	17.43	0.8000	0	1	1	5.75	7.6000	0	1	2	11.49	3.8000
0	1	3	10.91	3.4200	0	1	4	23.33	2.1300	0	1	5	5.97	3.1200
0	1	6	11.55	1.7400	0	1	7	17.23	1.3700	0	2	2	6.69	5.1300
0	2	3	6.83	4.2700	0	2	4	20.11	1.9500	0	2	5	6.31	2.8300
0	2	8	7.53	2.0100	0	2	9	17.92	1.1800	0	2	10	7.80	1.8300
0	2	11	10.54	1.3000	0	2	14	10.83	1.1100	0	3	5	12.26	1.7600
0	3	6	12.77	1.5800	0	3	7	17.76	1.3000	0	3	8	8.39	1.8600
0	3	9	12.83	1.3400	0	3	10	7.74	1.7700	0	3	11	14.49	1.0600
0	3	16	10.97	1.0600	0	4	4	25.15	1.6100	0	4	5	22.74	1.4500
0	4	7	20.85	1.2400	0	4	12	13.08	1.0800	0	4	14	8.85	1.3000
0	5	5	59.44	1.9500	0	5	6	28.00	1.2800	0	5	7	22.04	1.1900
0	5	8	8.81	1.7700	0	5	10	10.88	1.2600	0	5	11	21.42	0.9100
0	5	14	14.15	0.9400	0	6	6	34.21	1.2700	0	6	8	14.03	1.2500
0	6	11	23.86	0.8800	0	6	16	15.99	0.8100	0	7	7	11.78	1.4100
0	7	9	14.74	1.0700	0	7	10	9.81	1.3000	0	8	8	7.99	1.5900
0	10	10	10.20	1.1700	0	11	11	25.80	0.7500	0	11	16	12.09	0.9000
1	1	1	20.37	4.1400	1	1	3	33.43	2.8900	1	1	4	7.18	3.3800
1	1	5	10.46	2.0500	1	1	7	10.93	1.6300	1	1	8	11.59	1.5200
1	1	10	9.62	1.5700	1	2	2	31.72	3.1000	1	2	3	28.62	2.4600
1	2	4	11.92	2.2300	1	2	5	8.53	2.2600	1	2	7	12.66	1.5200
1	2	8	13.89	1.3800	1	2	9	8.02	1.8900	1	3	3	7.24	3.2500
1	3	7	22.00	1.2800	1	3	8	12.92	1.4100	1	3	9	9.68	1.6300
1	3	10	10.53	1.4000	1	4	6	14.32	1.4500	1	4	8	16.34	1.2200
1	4	14	9.82	1.2000	1	5	5	12.62	1.5300	1	5	7	12.20	1.4700
1	5	8	14.44	1.3000	1	5	10	8.37	1.5200	1	5	14	9.12	1.2500
1	6	8	12.07	1.3700	1	7	8	11.63	1.3100	1	8	10	8.22	1.4700
1	8	12	11.77	1.0500	1	9	9	8.70	1.4300	2	2	2	15.30	2.7800
2	2	3	24.46	2.1700	2	2	4	28.13	1.8500	2	2	5	28.70	1.6600
2	2	6	8.92	1.9600	2	2	8	9.53	1.7400	2	2	9	21.60	1.1400
2	2	10	8.20	1.7800	2	2	11	10.37	1.3100	2	2	15	11.37	1.0600
2	3	3	35.92	2.1500	2	3	4	8.86	2.2800	2	3	5	9.53	2.0800
2	3	6	6.80	2.3800	2	3	8	21.49	1.2100	2	3	9	8.84	1.7700
2	4	5	6.99	2.3600	2	4	7	21.62	1.2400	2	4	8	12.07	1.4200
2	5	6	10.25	1.6700	2	5	7	10.05	1.6500	2	5	8	9.12	1.7400
2	5	9	7.72	1.8100	2	5	11	10.56	1.2600	2	7	9	18.94	0.9800
2	7	14	10.13	1.1900	2	8	8	18.59	0.9800	2	9	12	11.25	1.1100
3	3	3	7.33	2.7600	3	3	4	20.01	1.5300	3	3	7	8.55	1.2900
3	3	8	42.92	1.3200	3	3	14	14.35	0.9600	3	4	4	21.57	1.4800
3	4	6	12.93	1.5100	3	4	7	25.15	1.2200	3	4	12	12.43	1.1200
3	5	6	13.32	1.4400	3	5	7	7.65	2.0500	3	6	6	11.58	1.5100
3	7	7	15.06	1.2100	3	7	9	16.65	1.0000	3	7	10	13.06	1.1200
3	8	8	24.59	0.9500	3	8	9	9.30	1.3300	3	8	14	12.59	1.0200
3	9	12	11.80	1.0800	4	4	4	14.47	1.5200	4	4	5	11.01	1.6800
4	4	8	12.87	1.3800	4	4	9	19.43	1.0700	4	4	11	13.83	1.1000
4	4	13	9.75	1.2700	4	4	14	10.21	1.2100	4	5	7	18.20	1.2100
4	5	11	9.18	1.3900	4	6	7	6.79	1.7500	4	7	7	16.39	1.1300
4	7	8	11.53	1.2800	4	8	10	9.52	1.3200	4	9	9	12.59	1.0800
4	11	12	9.75	1.1800	5	5	5	25.50	1.2200	5	5	6	18.14	1.2200
5	5	7	16.91	1.2200	5	5	8	12.93	1.2900	5	5	9	10.85	1.3100
5	5	10	8.91	1.4700	5	5	11	14.06	1.0900	5	6	6	19.91	1.1600
5	6	8	9.61	1.4700	5	6	11	18.81	0.9000	5	7	9	10.45	1.3100
5	7	10	11.34	1.1900	5	8	11	10.70	1.1700	5	8	12	10.89	1.1600
5	11	11	17.88	0.6400	6	6	6	18.79	1.1400	6	6	11	11.11	1.1600
6	7	10	8.68	1.4300	6	11	11	14.52	0.9300	7	7	9	18.59	0.9200
7	7	11	11.54	1.1300	7	7	14	11.94	1.0400	8	8	8	26.61	0.8400
8	8	14	12.03	1.0300	9	9	9	11.40	1.1600	9	9	9	-11.40	1.1600

2). PACKEM computer program output.

THIS IS CYCLE 4 OF SERIES 8 FOR ZN A C2H2 H2OS BACK ON 3FOLD, 4H2O AT .21 31 31
USING FOBS ABOVE 0.0 AND REFLECTIONS WITH SIN THETA/LAMBDA BELOW 1.4 10

H	K	L	SINL	KFOB	FCAL	COSA	SINA	DELTA	WT*RESIDSQ
0	0	1	0.041	64.25	117.65	1.0000	0.0	-53.40	[illegible]
0	0	2	0.082	17.79	29.66	-1.[illegible]	[illegible]	-11.87	1.8021
0	0	3	0.123	40.13	49.97	1.0000	0.0	-9.84	3.0976
0	0	4	0.165	31.94	27.97	1.0000	0.0	3.97	0.8641
0	0	5	0.206	57.16	73.47	1.[illegible]	0.0	-18.31	[illegible]
0	0	6	0.247	117.52	107.01	1.0000	0.0	10.51	5.6629
0	0	7	0.288	22.09	12.71	-1.0000	0.0	9.38	3.6781
0	0	8	0.329	36.94	31.21	[illegible]	0.0	5.73	5.2344
0	0	9	0.370	44.60	58.08	1.0000	0.0	-13.47	28.7670
0	0	10	0.411	78.25	78.47	1.0000	0.0	-0.23	0.[illegible]
0	0	11	0.453	49.14	54.27	1.0000	0.0	-5.14	7.9057
0	0	14	0.576	25.89	29.14	1.0000	0.0	-3.25	3.0622
0	0	16	0.658	33.15	34.42	1.[illegible]	[illegible]	-1.27	0.4844
0	1	1	0.058	10.90	21.82	-1.0000	0.0	-10.92	0.6728
0	1	2	0.092	21.79	21.37	-1.0000	0.0	0.42	0.0032
0	1	3	0.130	20.69	17.62	1.[illegible]	[illegible]	3.07	0.2244
0	1	4	0.170	44.24	29.37	-1.0000	0.0	14.87	[illegible]
0	1	5	0.210	31.32	4.97	-1.[illegible]	[illegible]	6.35	1.1500
0	1	6	0.250	21.90	20.08	1.0000	0.0	1.83	0.3040
0	1	7	0.291	32.68	35.20	-1.0000	0.0	-2.52	0.0417
0	2	2	0.116	12.69	11.16	-1.[illegible]	[illegible]	1.53	0.0246
0	2	3	0.148	12.95	2.90	-1.0000	0.0	10.05	1.5398
0	2	4	0.184	38.14	35.62	-1.0000	0.0	2.52	0.4629
0	2	5	0.222	31.97	18.79	-1.0000	0.0	-3.82	0.[illegible]
0	2	8	0.359	14.28	15.57	-1.0000	0.0	-1.29	0.1147
0	2	9	0.379	33.98	40.42	-1.[illegible]	[illegible]	-6.43	8.2685
0	2	10	0.420	14.79	17.13	-1.0000	0.0	-2.34	0.4527
0	2	11	0.460	19.99	19.28	1.0000	0.0	0.71	0.0833
0	2	14	0.582	20.54	21.76	-1.[illegible]	[illegible]	-1.22	0.3379
0	3	5	0.240	23.29	16.55	-1.0000	0.0	6.74	4.0751
0	3	6	0.276	24.22	32.45	1.0000	0.0	-8.23	7.5453
0	3	7	0.313	33.68	35.92	1.[illegible]	[illegible]	-2.24	0.8239
0	3	8	0.351	15.91	16.36	-1.0000	0.0	-0.45	0.0160
0	3	9	0.390	24.33	28.60	-1.0000	0.0	-4.27	2.8156
0	3	10	0.430	14.68	10.50	1.0000	0.0	4.18	1.5498
0	3	11	0.469	27.48	25.76	1.0000	0.0	1.72	0.7334
0	3	16	0.670	20.80	16.31	1.[illegible]	[illegible]	4.50	5.[illegible]
0	4	4	0.232	47.69	41.27	1.0000	0.0	6.42	4.4265
0	4	5	0.262	43.12	45.44	1.0000	0.0	-2.32	0.7114
0	4	7	1.332	39.54	37.40	-1.[illegible]	[illegible]	2.14	0.8345
0	4	12	0.520	24.81	24.09	-1.0000	0.0	0.72	0.1225
0	4	14	0.594	16.78	12.04	1.0000	0.0	4.74	3.7028
0	5	5	0.293	122.72	118.98	1.0000	0.0	3.73	0.[illegible]
0	5	6	0.321	53.10	47.46	1.0000	0.0	5.65	5.4257
0	5	7	0.354	41.80	41.63	-1.0000	0.0	0.17	0.0054
0	5	8	0.388	16.71	16.99	1.0000	0.0	-0.28	0.0070
0	5	10	0.460	20.63	21.83	1.[illegible]	[illegible]	-1.20	0.2526

3). FMLS computer program output (1/3).

2	5	8	0.397	37.30	19.36	1.0000	0.0	-2.04	0.3915
2	5	9	0.431	24.64	11.19	-1.0000	0.0	3.45	1.1121
2	5	11	0.504	20.03	18.03	1.0000	0.0	2.00	0.7003
2	7	9	0.476	35.92	35.48	1.0000	0.0	0.44	0.0565
2	7	14	0.649	19.21	16.59	1.0000	0.0	2.63	1.3531
2	8	8	0.473	35.25	34.21	-1.0000	0.0	1.04	0.3154
2	9	12	0.623	21.33	21.77	1.0000	0.0	-0.44	0.0430
3	3	3	0.214	13.95	19.37	-1.0000	0.0	-5.47	1.0908
3	3	4	0.240	37.95	43.17	1.0000	0.0	-5.22	3.0359
3	3	7	0.337	16.21	16.50	1.0000	0.0	-0.29	0.0265
3	3	8	0.373	81.39	75.35	-1.0000	0.0	6.04	5.8015
3	3	14	0.602	27.21	28.74	-1.0000	0.0	-1.53	0.7071
3	4	4	0.263	40.81	37.86	1.0000	0.0	2.95	1.1812
3	4	6	0.321	24.53	22.67	1.0000	0.0	1.85	0.4159
3	4	7	0.354	47.69	44.47	1.0000	0.0	3.22	1.3395
3	4	12	0.535	23.57	23.13	1.0000	0.0	0.45	0.0444
3	5	6	0.344	25.26	23.38	1.0000	0.0	1.88	0.4737
3	5	7	0.375	14.51	19.04	1.0000	0.0	-4.53	1.3606
3	6	6	0.371	21.96	26.49	1.0000	0.0	-4.53	2.0747
3	7	7	0.426	28.56	28.07	1.0000	0.0	0.55	0.0577
3	7	9	0.485	31.58	31.04	1.0000	0.0	0.54	0.0813
3	7	14	0.517	24.77	28.50	1.0000	0.0	-3.73	3.0303
3	8	8	0.482	46.63	49.75	-1.0000	0.0	-3.11	2.9876
3	8	9	0.511	17.44	13.77	-1.0000	0.0	3.86	2.1785
3	8	14	0.675	23.88	28.51	-1.0000	0.0	-4.64	5.7457
3	9	12	0.629	22.33	16.05	1.0000	0.0	6.32	9.5345
4	4	4	0.285	27.44	29.85	1.0000	0.0	-2.41	0.6903
4	4	5	0.317	20.86	14.03	-1.0000	0.0	6.85	4.6238
4	4	8	0.403	24.41	24.91	1.0000	0.0	-0.51	0.0276
4	4	9	0.437	36.85	41.50	1.0000	0.0	-4.65	5.2467
4	4	11	0.509	26.23	24.64	-1.0000	0.0	1.58	0.5755
4	4	13	0.583	18.49	17.43	1.0000	0.0	1.06	0.1345
4	4	14	0.622	19.36	21.48	1.0000	0.0	-2.12	0.8504
4	5	7	0.390	34.51	33.12	-1.0000	0.0	1.39	0.3676
4	5	11	0.524	17.41	12.73	-1.0000	0.0	4.68	3.1437
4	6	7	0.473	16.67	11.16	-1.0000	0.0	5.51	3.7294
4	7	7	0.439	31.08	29.65	1.0000	0.0	1.43	0.4460
4	7	8	0.467	21.67	21.11	1.0000	0.0	0.56	0.1244
4	8	10	0.552	18.05	12.06	1.0000	0.0	5.99	5.7796
4	9	9	0.549	23.88	22.07	1.0000	0.0	1.81	1.7814
4	11	12	0.696	18.49	7.47	-1.0000	0.0	11.02	24.2335
5	5	5	0.356	48.36	45.51	1.0000	0.0	2.85	1.2136
5	5	6	0.382	34.40	34.10	1.0000	0.0	0.30	0.1166
5	5	7	0.409	32.07	31.35	-1.0000	0.0	0.71	0.0985
5	5	8	0.439	24.52	24.67	1.0000	0.0	-0.29	0.0141
5	5	9	0.471	21.58	20.61	1.0000	0.0	-0.03	0.0002
5	5	10	0.504	16.90	18.55	1.0000	0.0	-1.65	0.3499
5	5	11	0.538	26.66	26.42	1.0000	0.0	0.24	0.0150
5	6	6	0.415	37.76	34.24	1.0000	0.0	3.52	2.5613
5	6	8	0.460	18.22	18.35	1.0000	0.0	-0.12	0.0019
5	6	11	0.555	35.67	34.05	1.0000	0.0	1.63	0.9877
5	7	9	0.512	19.82	22.71	-1.0000	0.0	-2.89	1.3544
5	7	10	0.543	21.51	25.38	-1.0000	0.0	-3.87	2.9441
5	8	11	0.586	20.29	24.97	1.0000	0.0	-4.67	5.0178
5	8	12	0.628	20.65	17.38	1.0000	0.0	3.27	2.3055
5	11	11	0.672	33.91	34.74	1.0000	0.0	-0.83	0.2720
6	6	6	0.428	35.63	26.81	-1.0000	0.0	8.82	16.6544
6	6	11	0.572	21.07	25.23	1.0000	0.0	-4.16	3.5788
6	7	10	0.560	16.46	8.03	-1.0000	0.0	8.43	9.6594
6	11	11	0.686	27.54	23.65	1.0000	0.0	3.89	4.3558
7	7	9	0.550	35.25	33.67	1.0000	0.0	1.58	0.8214
7	7	11	0.603	21.88	18.94	-1.0000	0.0	2.91	1.8333
7	7	14	0.705	22.64	20.74	1.0000	0.0	1.91	0.9349
8	8	8	0.570	50.46	52.01	-1.0000	0.0	-1.54	0.9303
8	8	14	0.747	22.81	22.35	-1.0000	0.0	0.46	0.0562
9	9	9	0.641	21.67	22.60	1.0000	0.0	-0.86	0.1793

3). FMLS computer program output (2/3).

6	7	10	0.590	16.46	8.03	-1.0000	0.0	8.43	9.6584
6	11	11	0.686	27.54	23.65	1.0000	0.0	3.89	4.8558
7	7	9	0.550	35.25	33.67	1.0000	0.0	1.58	0.8214
7	7	11	0.609	21.89	18.98	-1.0000	0.0	2.91	1.8333
7	7	14	0.705	22.64	20.74	1.0000	0.0	1.91	0.9349
6	8	8	0.570	50.46	52.01	-1.0000	0.0	-1.54	0.9383
6	8	14	0.743	22.81	22.35	-1.0000	0.0	0.46	0.0562
9	9	9	0.641	21.62	22.50	1.0000	0.0	-0.88	0.1593

B 4 ZN A C2H2 H2OS BACK ON 3FOLD, 4H2O AT .31 31 31

DIAGONAL ELEMENTS OF NORMAL EQUATION MATRIX

PARAMETER 1 (SCALE, G), 29692.

X-X	Y-Y	Z-Z	B11-B11	B22-B22	B33-B33	B12-B12	B13-B13	B23-B23
7254260.	1.	1.	44975824.	1.	1.	5332971.	1.	1.

X-X	Y-Y	Z-Z	B-B
1.	7506961.	12721224.	12?2.142
1.	465938.	1.	12.680
1.	1356242.	1.	16.216
1618937.	1.	820194.	15.416
1.	1.	1.	14.584
64505.	1.	1.	0.343
147644.	1.	1.	0.967

DELTA G (SCALE FOR FCALC) IS-0.00020, WEIGHTED SUM OF SQUARES OF RESIDUALS IS 406.73496

DELTA X	DELTA Y	DELTA Z	DELTA B11	DELTA B22	DELTA B33	DELTA B12	DELTA B13	DELTA B23
0.000002	0.000002	0.000002	0.000001	0.000001	0.000001	0.000001	0.000001	0.000001

DELTA X	DELTA Y	DELTA Z	DELTA B OR OCC
0.0	0.000016	-0.000014	0.0008
0.0	-0.000019	0.0	0.0008
0.0	0.000066	0.000066	0.0026
0.000191	0.000191	-0.000119	-0.0324
0.0	0.0	0.0	0.0024
-0.000286	-0.000286	-0.000286	-0.2930
-0.000569	-0.000569	-0.000569	0.1593

SUM FOBS = 5168.180, SUM /DEL F/ = 625.221, R =0.12098, NO. OF REFL. IN L.S. = 179, SLMX = 1.4000

THE GENERALIZED WEIGHTED R INDEX (R2) = 0.11625

NORMALIZED SUM OF SQUARES OF RESIDUALS = 14.428. SQ RT OF SUM (WTD RESIDS SQ)/(# OF EXCESS OBS) = 1.594.
(GOODNESS OF FIT)

NEW SCALE FACTOR FOR FOBS = 1.89679. THIS IS (OLD SCALE FACTOR) TIMES G/(G + DELTA G). G IS NOT CHANGED.

ATOM	NEW X	NEW Y	NEW Z	B11 OR B	B22 OR OCC	NEW B33	NEW B12	NEW B13	NEW B23
1	0.213381	0.213381	0.213381	0.003385	0.003385	0.003385	0.003763	0.003763	0.003763 ZN1
2	0.0	0.381563	0.366759	0.8345	0.500000	SIAL			
3	0.0	0.201426	0.500000	2.4735	0.250000	O(1)			
4	0.0	0.591382	0.391382	1.9743	0.250000	O(2)			
5	0.118823	0.118823	0.325250	3.9127	0.500000	O(3)			
6	0.0	0.0	0.0	3.3782	0.020833	ZN(2			
7	0.083175	0.083175	0.083175	6.6943	0.083333	HE01			
8	0.306486	0.306486	0.306486	4.2901	0.083333	H202			

3). FMLS computer program output (3/3).

ZN-A HYDRATED NOV. 27, 1972

ORTHOGONAL COORDINATES OF ALL ATOMS

ATOM	X COORD	Y COORD	Z COORD
O1	0.0	6.09800	2.53869
SIAL	0.0	4.49340	3.22406
O2	0.0	3.61478	2.61479
O3	1.36462	4.03533	1.36431
O3	-1.36386	4.03533	1.36386
SIAL	0.0	7.70060	2.22406
SIAL	0.0	3.22406	4.49340
SIAL	2.22406	4.49340	0.0
O3	1.36427	1.36456	4.03467
H2O1	0.89153	1.31362	1.31362
ZN1	2.56681	2.56681	2.56681
H2O3	3.90302	3.90302	3.90302
H2O2	3.42242	3.42242	3.42242
H2O6	4.46497	6.09800	6.09800
H2O5	2.85723	6.09800	6.09800
H2O7	3.09064	3.71322	6.09800
H2O7	3.09064	8.47678	6.09800
H2O4	6.09800	2.55109	4.63219
H2O4	4.63219	6.09800	2.55109
H2O4	6.09800	2.55109	7.56381
O1	6.09800	0.0	2.53869
O2	3.61478	0.0	3.61478
O1	0.0	6.09800	2.53869
O1	0.0	2.53869	6.09800
H2O1	-0.89153	-1.31362	1.31362

THE INPUT STANDARD DEVIATIONS FOR THE FOLLOWING ATOM WERE ZERO. THE OUTPUT STANDARD DEVIATIONS INVOLVING IT ARE NONSENSE.

ZN2	0.0	0.0	0.0
O3	4.02653	1.35749	1.36451
H2O4	6.09800	2.55109	4.63219

4). MGEOM computer program output (1/2).

ATOM A	ATOM B	ATOM C	BOND AB	BOND BC	ANG ABC	ST D AB	ST D BC	ST D ABC
O1	SIAL	O2	1.63516	1.64501	111.134	0.00555	0.00573	0.698474
O1	SIAL	O3	1.63516	1.67671	111.554	0.00555	0.00670	0.707781
O2	SIAL	O3	1.64501	1.67671	106.718	0.00573	0.00670	0.856762
O3	SIAL	O3	1.67671	1.67441	103.821	1.00673	0.00670	1.170050
SIAL	O1	SIAL	1.63516	1.63916	157.372	0.00555	0.00555	0.931436
SIAL	O2	SIAL	1.64501	1.64501	154.367	0.00573	0.00573	1.188423
SIAL	O3	SIAL	1.67671	1.67513	139.470	0.00670	0.00670	1.195855
O3	H201	O3	2.76304	2.76248	86.245	0.04976	0.04976	2.150603
O3	ZN1	O3	2.24642	2.24633	114.437	0.00838	0.00838	1.326816
O3	H203	O3	3.50259	3.50257	63.427	0.00076	0.00077	2.026479
O3	H202	O3	2.97433	2.97423	78.533	0.04256	0.04240	1.436609
H201	ZN1	H203	2.43704	2.31613	171.379	0.06967	0.12911	0.956627
H205	H205	H207	2.36226	2.38332	96.359	0.12075	0.11681	2.362117
H207	H205	H207	2.38332	2.38332	167.362	0.11681	0.11681	4.302417
O2	H206	H205	3.54245	2.36226	37.542	0.01827	0.11079	0.488228
O1	H206	O1	3.58955	3.58955	89.038	0.02340	0.02340	0.400167
ZN1	H203	H204	2.31613	2.67905	109.805	0.12911	0.14615	1.772891
H204	H203	H204	2.67905	2.67905	109.136	0.06615	0.06615	3.633126
H204	H204	H203	2.93163	2.67905	105.794	0.18423	0.06615	2.349707
O1	H204	O2	3.33311	3.71263	45.015	0.00466	0.17681	1.102584
O1	H204	H203	3.30011	2.67905	103.559	0.00965	0.06615	3.362947
O1	H207	H205	3.30842	2.38332	104.587	0.11555	0.11681	2.423315
O1	H207	H206	3.30842	3.54208	63.731	0.11555	0.13794	1.299302
O3	ZN1	H203	2.24609	2.31613	102.887	0.01838	0.12911	2.364486
O3	ZN1	H201	2.24609	2.43704	72.166	0.01838	0.04967	1.116483
O3	H201	ZN2	3.76248	2.06058	135.543	0.04976	0.01838	3.204603
H204	H202	H207	3.06291	2.71235	75.426	0.06661	0.05287	2.764632
H204	H203	H207	2.67905	2.34779	89.439	0.06615	0.05484	3.215753

4). MGEOM computer program output (2/2).

APPENDIX C

Chemicals Utilized

1. acetylene	99.6% pure, Matheson, Coleman & Bell
2. calcium nitrate	crystals, Mallinckrodt Chemical Works
3. chromic nitrate	reagent crystals, Matheson, Coleman & Bell
4. cobalt nitrate	Matheson, Coleman & Bell
5. cupric nitrate	J.T.Baker Chemical Company
6. gold cloride	reagent grade, Merck Company
7. ferrous sulfate	J.T.Baker Chemical Company
8. manganese perchlorate	The G.Frederick Smith Chemical Company
9. selenium	powder, A.D.Mackay Inc.
10. silver nitrate	reagent crystals, Matheson, Coleman & Bell
11. sodium aluminate	Research Organic/Inorganic Chemical Corp.
12. sodium metasilicate	Research Organic/Inorganic Chemical Corp.
13. tellurium	99.5% pure powder, Matheson, Coleman & Bell
14. triethanolamine	Matheson, Coleman & Bell
15. zeolite A	powder, Linde Company
16. zinc nitrate	crystals, Mallinckrodt Chemical Works

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